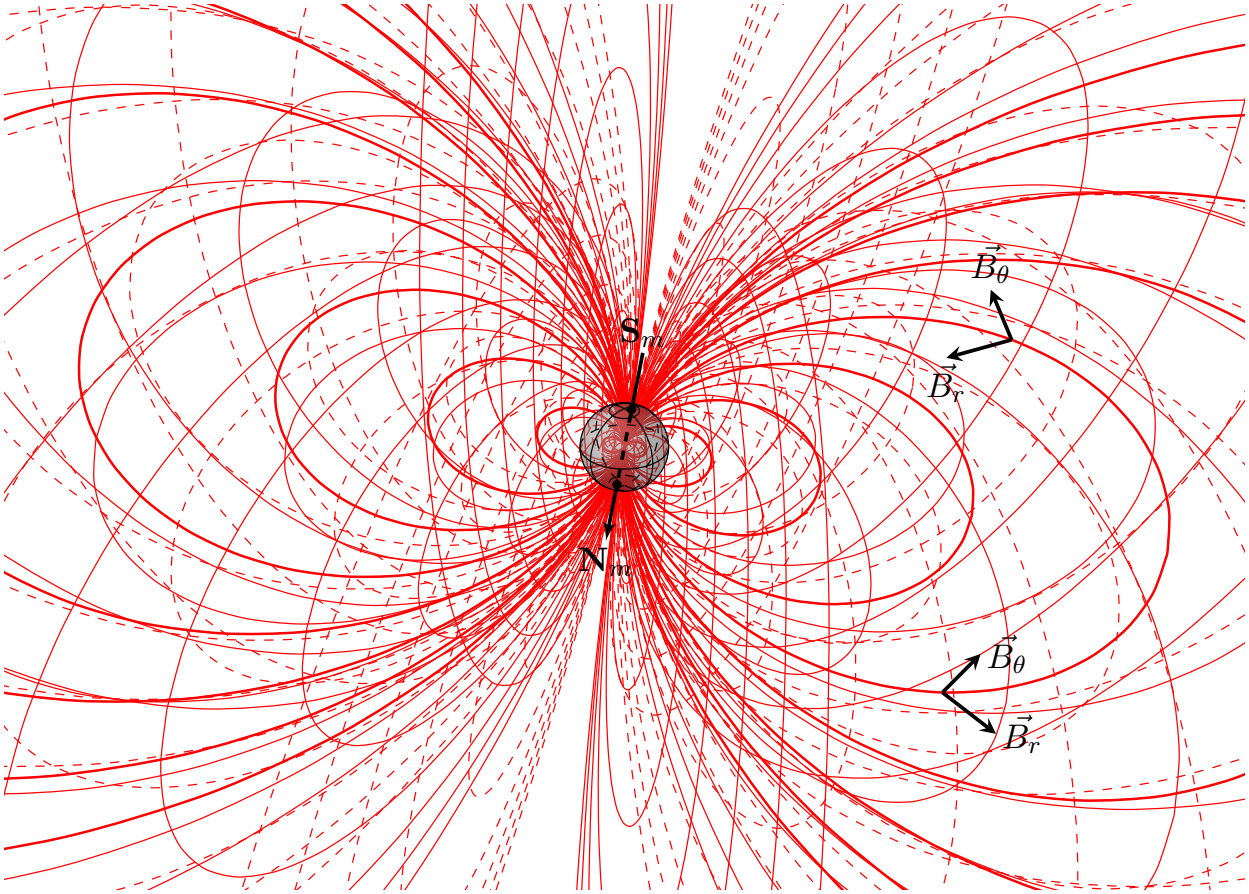
Lecture and Exercise Notes:

Theoretical Chemistry

Introduction to Theoretical Methods for Describing Electronic Structure, Spectroscopy, and Linear and Nonlinear Electro-optical Properties

Robert W. Góra



Dipolar magnetic field plot by Cyril Langlois taken from texample.net

Electronic structure of atoms and molecules

Summary

The lecture and exercise notes are supplementary material for participants in the *"Theoretical Chemistry"* course. The aim of the course is to introduce the concepts of the theory of electronic structure of molecular systems and theoretical methods for determining their properties.
The initial chapters discuss the fundamental approximations of molecular quantum mechanics. This material is based on the textbooks of Atkins and Friedman[1], Engel[2], and the monograph by May and Kühn.[3] Calculation exercises are based on the monograph by Szabo and Ostlund.[4]
The materials contain figures that are subject to copyright and are intended for internal use only by students of the Theoretical Chemistry course.

Robert W. Góra
Wrocław, 2026.06.10

[1] P. W. Atkins and R. Friedman, *Molecular quantum mechanics*, 5th ed. Oxford ; New York: Oxford University Press, 2011.

[2] T. Engel and P. Reid, *Quantum Chemistry and Spectroscopy*, 3rd ed. Boston: Pearson, 2013.

[3] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems*, 3rd. Wiley-VCH Verlag GmbH & Co. KGaA, 2011.

[4] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, Courier Corporation, June 2012.

Contents

Classical Mechanics **5**

Postulates of Non-Relativistic Quantum Mechanics **11**
2.1 Postulates . . . 11
2.2 Spin . . . 23
2.3 Unitary operators . . . 25
2.4 Generators . . . 26
2.5 Schrödinger Equation . . . 29
2.6 Free Particle . . . 32
2.7 Particle in a Potential Box . . . 34

Electronic and vibrational molecular states **39**
3.1 Time-(in)dependent Schrödinger equation . . . 39
3.2 Molecular Hamiltonian . . . 40
3.3 Born–Oppenheimer Separation . . . 40
3.4 Potential energy surfaces . . . 42
3.5 Born–Oppenheimer Approximation . . . 42
3.6 Harmonic approximation . . . 43
3.7 Normal mode analysis . . . 45
3.8 Hamiltonian in diabatic representation . . . 54

Electronic structure calculation methods **59**
4.1 Variational Method . . . 59
4.2 Molecular Orbital Method . . . 60
4.3 Perturbation Theory . . . 64
4.4 Determinantal Wave Function . . . 67
4.5 Hartree–Fock Method . . . 72
4.6 Molecular Orbitals . . . 78
4.7 Configuration Interaction . . . 81
4.8 Møller–Plesset Partitioning . . . 85
4.9 Coupled clusters . . . 88
4.10 Density Functional Theory . . . 93
4.11 Electronic Excitations in the RPA Paradigm . . . 102

Computational Chemistry **110**
5.1 Chemical Accuracy . . . 110
5.2 Good Practices in KS-DFT . . . 110
5.3 Good Practices in WFT . . . 118

Light-matter interaction **128**
6.1 The Jablonski diagram . . . 128
6.2 The Golden Rule . . . 128
6.3 Interaction with external field . . . 130
6.4 One-photon absorption . . . 132

Intermolecular Interactions **137**
7.1 Intermolecular Interactions . . . 137

Theory of nonlinear optical phenomena **143**
8.1 Nonlinear optical properties 143
8.2 Time-dependent polarization 146
8.3 Nonlinear optical processes 147
8.4 Time-dependent perturbation theory 147
8.5 Molecular (hyper)polarizabilities 150
8.6 Clamped nuclei approximation 151
8.7 Vibrational contributions 152
8.8 Computational approaches for estimation of molecular (hyper)polarizabilities 153

References **157**

Chapter 1
Classical Mechanics

1.1

A Brief Introduction to Lagrangian and Hamiltonian Mechanics

- Newtonian mechanics is based on forces and Newton's second law.
- Lagrangian and Hamiltonian mechanics rely on the *principle of least action*.
- It facilitates the analysis of systems with constraints and forms a bridge to quantum mechanics.
- Fundamental quantities:
  - Lagrangian $L = T - V$,
  - Hamiltonian $H = T + V$,
  - Action $S = \int L\,dt$.

1.2

Principle of Least Action

$$\delta S = 0, \quad S = \int_{t_1}^{t_2} L(q, \dot{q}, t)\, dt$$

- The actual trajectory minimizes (more precisely: extremizes) the action.
- q — generalized coordinates, $\dot{q}$ — generalized velocities.
- The condition $\delta S = 0$ leads to the Euler–Lagrange equations:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$$

1.3

Example

Consider a simple example of a particle in a one-dimensional potential:

$$L = \frac{mv^2}{2} - V(x) = \frac{m\dot{q}^2}{2} - V(q)$$

Substitute the above L into the Euler–Lagrange equations:

$$\begin{aligned}
&\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0 \\
&\frac{d}{dt}(m\dot{q}) + \frac{\partial V(q)}{\partial q} = 0 \\
&m\ddot{q} = -\frac{\partial V(q)}{\partial q} \quad \rightsquigarrow \quad F = -\nabla V
\end{aligned}$$

The Lagrangian formalism does not require introducing forces explicitly—everything follows from the scalar potential.

Hamiltonian Formalism

- Transition from velocities to momenta:

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

- Hamiltonian:

$$H(q,p,t) = \sum_i p_i \dot{q}_i - L$$

- Hamilton's equations:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

- A system of first-order equations—often more convenient for numerical solutions.

Legendre Transform — Geometric Interpretation

Let $f(x)$ be a convex function. Define the slope:

$$s = \frac{df}{dx}$$

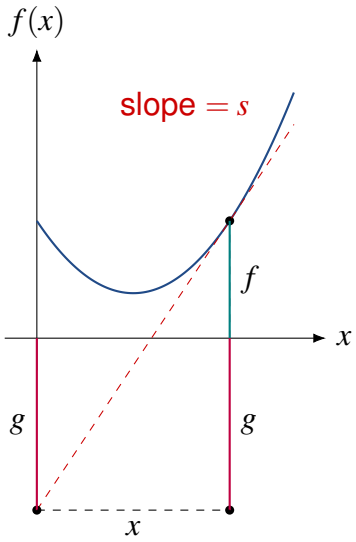
The Legendre transform of $f(x)$ is

$$g(s) = sx - f(x)$$

Geometrically:

- Draw the tangent line with slope s.
- sx is the height of the tangent line.
- $g(s)$ is the vertical intercept.

$$\frac{f+g}{x} = s \;\rightsquigarrow\; g = sx - f$$



1.6

Example: Harmonic Oscillator

- Generalized coordinate: x
- Equilibrium position: $x = 0$
- Kinetic energy:

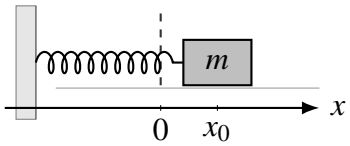
$$T = \frac{1}{2} m \dot{x}^2$$

- Potential energy:

$$V = \frac{1}{2} k x^2$$

- Equation of motion:

$$m\ddot{x} + kx = 0 \quad \rightsquigarrow \quad \ddot{x} + \omega^2 x = 0$$



1.7

Equations of Motion of the Oscillator

Ansatz: $x(t) = A\cos(\omega t) + B\sin(\omega t)$ where $\omega^2 = \frac{k}{m}$. Indeed, if we substitute this solution into

$$\frac{d^2x}{dt^2} = -\omega^2 x$$

we obtain

$$\frac{d}{dt}(-A\omega\sin(\omega t) + B\omega\cos(\omega t)) = -\omega^2 x(t)$$

Now impose the initial conditions:

$$\begin{cases} x(0) = x_0 & \rightsquigarrow A = x_0 \\ \dfrac{dx}{dt}(0) = 0 & \rightsquigarrow B = 0 \end{cases}$$

Hence

$$\boxed{x(t) = x_0\cos(\omega t)}$$

1.8

Harmonic Oscillator — Lagrangian Formalism

Generalized coordinate:

$$q = x$$

Lagrangian:

$$L = T - V = \frac{1}{2}m\dot{x}^2 - \frac{1}{2}kx^2$$

Euler–Lagrange equation:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) - \frac{\partial L}{\partial x} = 0$$

leads to the equation of motion:

$$m\ddot{x} + kx = 0$$

1.9

Harmonic Oscillator — Hamiltonian Formalism

- Hamiltonian:

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

  where

$$p = \frac{\partial L}{\partial \dot{x}} = m\dot{x}$$

- Hamilton's equations:

$$\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m} \qquad \text{or} \qquad p = m\frac{dx}{dt}$$

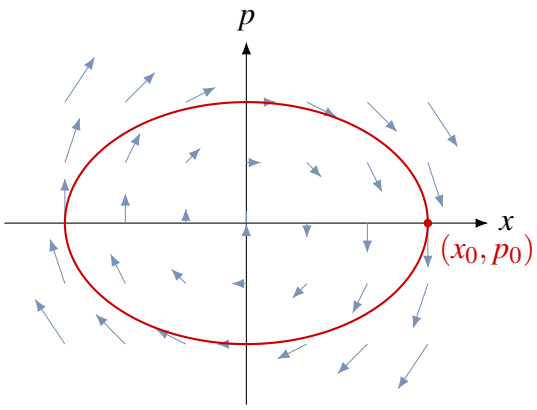
$$\dot{p} = -\frac{\partial H}{\partial x} = -kx \qquad\qquad \frac{dp}{dt} = -kx$$

- Combining the equations yields the same equation of motion (substitute $\dot{p} = m\ddot{x}$ into the second equation and divide by m to obtain $\ddot{x} + \frac{k}{m}x = 0$).

1.10

Phase Space — Harmonic Oscillator

$$\frac{d}{dt}\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} p/m \\ -kx \end{pmatrix}$$



Vector field: $\dot{x} = \frac{p}{m}$, $\dot{p} = -kx$. The red curve is the trajectory at constant energy—an ellipse $\frac{x^2}{2E/k} + \frac{p^2}{2mE} = 1$.

1.11

Example: Simple Pendulum

- Generalized coordinate: $q = \theta$
- Kinetic energy:

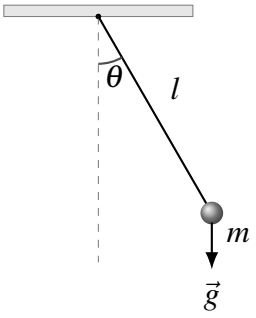
$$T = \frac{1}{2} m l^2 \dot{\theta}^2$$

- Potential energy:

$$V = mgl(1 - \cos\theta)$$

- Lagrangian:

$$L = T - V = \frac{1}{2} m l^2 \dot{\theta}^2 - mgl(1 - \cos\theta)$$



1.12

Equations of Motion of the Pendulum

$$\frac{d}{dt}\left(ml^2\dot{\theta}\right) + mgl\sin\theta = 0$$

$$\Rightarrow \ddot{\theta} + \frac{g}{l}\sin\theta = 0$$

- Nonlinear equation of motion.
- For small oscillations $\sin\theta \approx \theta$:

$$\ddot{\theta} + \frac{g}{l}\theta = 0$$

— simple harmonic motion.

1.13

Lagrangian Formalism — Simple Pendulum

- Generalized coordinate:

$$q = \theta$$

- Kinetic energy:

$$T = \frac{1}{2} m (l\dot{\theta})^2 = \frac{1}{2} m l^2 \dot{\theta}^2$$

- Potential energy:

$$V = mgl(1 - \cos\theta)$$

- Lagrangian:

$$L = T - V = \frac{1}{2} m l^2 \dot{\theta}^2 - mgl(1 - \cos\theta)$$

- Euler–Lagrange equation:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right) - \frac{\partial L}{\partial \theta} = 0$$

- Equation of motion:

$$\ddot{\theta} + \frac{g}{l}\sin\theta = 0$$

$\sin\theta \approx \theta$ for small oscillations — simple harmonic motion

1.14

Solution of the Equation of Motion — Simple Pendulum (Lagrange)

- Equation of motion:

$$\ddot{\theta} + \frac{g}{l}\sin\theta = 0$$

- For small oscillations: $\sin\theta \approx \theta$

$$\ddot{\theta} + \omega_0^2\theta = 0 \qquad \text{where } \omega_0 = \sqrt{\frac{g}{l}}$$

- General solution:

$$\theta(t) = \Theta_0 \cos(\omega_0 t + \varphi)$$

- The equation describes simple harmonic motion with angular frequency ω_0 and amplitude Θ_0.
- Period:

$$T = \frac{2\pi}{\omega_0} = 2\pi\sqrt{\frac{l}{g}}$$

1.15

Solution of the Equation of Motion — Simple Pendulum (Hamilton)

- Generalized variable: $q = \theta$, generalized momentum:

$$p_\theta = ml^2\dot{\theta}$$

- Hamiltonian:

$$H = \frac{p_\theta^2}{2ml^2} + mgl(1-\cos\theta)$$

- Hamilton's equations:

$$\dot{\theta} = \frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{ml^2} \qquad \dot{p_\theta} = -\frac{\partial H}{\partial \theta} = -mgl\sin\theta$$

- For small oscillations: $\sin\theta \approx \theta$

$$\dot{p_\theta} = -mgl\theta \qquad \Rightarrow \qquad \ddot{\theta} + \frac{g}{l}\theta = 0$$

- Solution:

$$\theta(t) = \Theta_0\cos(\omega_0 t + \varphi), \qquad p_\theta(t) = -ml^2\omega_0\Theta_0\sin(\omega_0 t + \varphi)$$

1.16

Chapter 2
Postulates of Non-Relativistic Quantum Mechanics

2.17

2.1 Postulates

How to determine the state of a quantum-mechanical system?
The state of a system with f degrees of freedom is specified by the wave function $\Psi = \Psi(r_1, r_2, \ldots, r_f, t)$, which depends on the generalized coordinates r_i and time t. We will denote these coordinates collectively by the vector $\vec{r}$:

$$\Psi = \Psi(\vec{r}, t)$$

2.18

Max Born's statistical interpretation

The product of the square of the wave function's modulus and the volume element $d\tau$ gives the probability that at time t the system is found in the volume element $d\tau$ indicated by $\vec{r}$.

$$p(\vec{r}, t) = \Psi^*(\vec{r}, t)\Psi(\vec{r}, t)\, d\tau$$

For a single particle[a] the probability of finding it anywhere must be equal to unity, hence:

$$\int_\tau \Psi^*(\vec{r}, t)\Psi(\vec{r}, t)\, d\tau = 1$$

[a] By convention, many-particle wave functions are usually normalized to 1

2.19

Example 1
What if the normalization condition is not satisfied?

$$\int_\tau \psi^*(\vec{r},t)\,\psi(\vec{r},t)\,d\tau = A$$

Because the Schrödinger equation is linear, if ψ is a solution, then $N\psi$ will also be a solution. We simply multiply our function ψ by an appropriate constant N so that the condition becomes satisfied:

$$\int_\tau \left[N\psi(\vec{r},t)\right]^* N\psi(\vec{r},t)\,d\tau = A|N|^2 = 1$$

thus

$$N = \pm\frac{1}{\sqrt{A}}\ldots \text{or } N = e^{i\phi}\frac{1}{\sqrt{A}}, \text{ etc.}$$

2.20

Quantum States as Vectors

- A quantum state is represented by a vector $|\psi\rangle$ in the complex Hilbert space $\mathscr{H}$, which contains information about the mechanical quantities of the system (their values and the corresponding probabilities).
- For example, for a discrete spectrum of energy eigenstates, a quantum state is represented by a linear combination (superposition):

  $$|\psi\rangle = c_1|E_1\rangle + c_2|E_2\rangle + c_3|E_3\rangle + \cdots = \sum_i c_i|E_i\rangle$$

  where the coefficients c_i determine the probability of measuring a given value.
- The same quantum state can also be written in terms of possible angular-momentum values (or another mechanical quantity):

  $$|\psi\rangle = a_1|L_1\rangle + a_2|L_2\rangle + a_3|L_3\rangle + \cdots = \sum_i a_i|L_i\rangle$$

2.21

- However, not all quantities in quantum mechanics are discrete—for example, the position of an electron. How do we write the state of the system then?

  $$|\psi\rangle = b_1|x_1\rangle + b_2|x_2\rangle + b_3|x_3\rangle + \cdots$$

- Since the possible positions $|x_i\rangle$ vary continuously:

  $$|\psi\rangle = \int dx\, b(x)\,|x\rangle$$

  where $b(x)$ is in fact the wavefunction in the position representation, which is in a sense a list of coefficients in front of each possible position vector.

2.22

Why Do We Need a Hilbert Space?

- Quantum mechanics describes the states of a system as **vectors** in a complex space, which can be added and scaled linearly.
- We need a structure that:
  - allows us to measure "lengths" and "angles" (i.e., amplitudes and probabilities),
  - ensures completeness—every convergent sequence of states has a physical meaning,
  - enables the representation of observable operators and time evolution.
- Such a structure is a **Hilbert space** $\mathscr{H}$, a complete vector space with an inner product $\langle\cdot|\cdot\rangle$.
- Thanks to this:
  - the inner product yields the Born rule: $p = |\langle\phi|\psi\rangle|^2$,
  - Hermitian operators represent observables,
  - unitary operators describe evolution and changes of basis.

2.23

Inner Product

- In Cartesian space, the dot product measures the angle between vectors:
$$\vec{v}\cdot\vec{w} = v_1w_1 + v_2w_2 + v_3w_3 + \cdots = |\vec{v}||\vec{w}|\cos\theta$$
- it also allows us to determine the length of a vector:
$$|\vec{v}| = \sqrt{\vec{v}\cdot\vec{v}}$$
- the inner product is a generalization of the dot product mapping vectors to scalars:
$$\langle\psi|\phi\rangle = c$$
$$\langle\psi|\xi+\phi\rangle = \langle\psi|\xi\rangle + \langle\psi|\phi\rangle$$
$$\langle\psi|a\phi\rangle = a\langle\psi|\phi\rangle$$
$$\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*$$

2.24

- The inner product will be a measure of the weight of a given state in a superposition (probability amplitude):
$$|\psi\rangle = \sum_i c_i|E_i\rangle$$
$$\langle E_2|\psi\rangle = \langle E_2|\sum_i c_i|E_i\rangle = \sum_i c_i\langle E_2|E_i\rangle$$
for an orthonormal basis
$$\langle E_i|E_j\rangle = \delta_{ij} = \begin{cases} 1, & \text{if } i = j, \\ 0, & \text{if } i \neq j. \end{cases}$$
where δ_{ij} is the so-called Kronecker delta, therefore
$$\langle E_2|\psi\rangle = \sum_i c_i\delta_{2i} = c_2\delta_{22} = c_2$$

2.25

Consider the inner product of two functions

$|\psi\rangle$ and $|\phi\rangle$ represent the state of the system as a superposition of discrete energy eigenstates

$$\langle\psi|\phi\rangle = \Big(\sum_i a_i^* \langle E_i|\Big)\Big(\sum_j b_j |E_j\rangle\Big) = \sum_i\sum_j a_i^* b_j \langle E_i|E_j\rangle = \sum_i\sum_j a_i^* b_j \delta_{ij} = \sum_i a_i^* b_i$$

for real coefficients $\{a_i\}$ and $\{b_i\}$ we obtain the dot product in $\mathbb{R}^n$

2.26

Inner Product for Continuous Linear Combinations

- Similarly to the discrete case, we want to obtain the coefficient corresponding to a given position:

$$\langle x_2|\psi\rangle = \langle x_2| \int dx\, b(x)\, |x\rangle$$
$$\int dx\, b(x)\, \langle x_2|x\rangle = b(x_2)$$

for this purpose we use a special function, the so-called Dirac delta $\delta(x)$:

$$b(x_2) = \int dx\, b(x)\delta(x_2 - x)$$

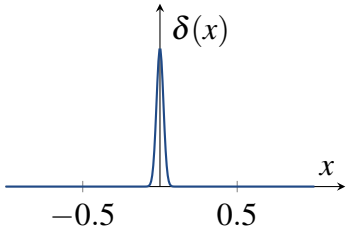
by definition, the only nonzero contribution of δ occurs at the point x_2, hence:

$$\int dx\, b(x_2)\delta(x_2 - x_2) = b(x_2)\underbrace{\int dx\, \delta(x_2 - x_2)}_{1} = b(x_2)$$

2.27

Properties of the Dirac Delta Function

The function $\delta(x)$ is an idealized function concentrated at the point $x = 0$. Formally: $\delta(x) = 0$ for $x \neq 0$ and $\int_{-\infty}^{\infty} \delta(x)\, dx = 1$



- Sampling property:

$$\int_{-\infty}^{\infty} f(x)\delta(x - x_0)\, dx = f(x_0)$$

- For example, a “narrow” Gaussian:

$$\delta(x) = \lim_{a\to 0} \frac{1}{a\sqrt{2\pi}} e^{-\frac{x^2}{2a^2}}$$

but equally well:

$$\lim_{a\to 0} \frac{1}{x\pi} \sin\left(\frac{x}{a}\right)$$

2.28

- Similarly to the discrete case, we want to obtain the coefficient corresponding to a given position:

$$\langle x_2|\psi\rangle = \langle x_2| \int dx\, b(x)\, |x\rangle$$
$$\int dx\, b(x)\, \langle x_2|x\rangle = b(x_2)$$

for this purpose we use a special function, the so-called Dirac delta $\delta(x)$:

$$b(x_2) = \int dx\, b(x)\delta(x_2 - x)$$

2.29

Consider the inner product of two functions
$|\psi\rangle$ and $|\phi\rangle$ represent the state of the system as a superposition of continuous positions

$$\langle\psi|\phi\rangle = \left(\int dx\, \psi(x)\, \langle x|\right) \left(\int dy\, \phi(y)\, |y\rangle\right) =$$
$$\iint dxdy\, \psi^*(x)\phi(y)\, \langle x|y\rangle =$$
$$\iint dxdy\, \psi^*(x)\phi(y)\delta(x-y) =$$
$$\int dx\, \psi^*(x)\phi(x)$$

As you can see, in this case the inner product is given by an integral of the product of the functions. Therefore, such an integral is often called a scalar product.

2.30

Examples

Normalization of a state vector
The state is given by:

$$|\psi\rangle = 2|E_1\rangle - i|E_2\rangle + |E_3\rangle$$

Calculate the norm and normalize this state. Compute the probability of measuring E_2. Norm:

$$\langle\psi|\psi\rangle = |2|^2 + |-i|^2 + |1|^2 = 4 + 1 + 1 = 6$$

Normalized state:

$$|\psi\rangle_{\text{norm}} = \frac{1}{\sqrt{6}}\left(2|E_1\rangle - i|E_2\rangle + |E_3\rangle\right)$$

Probability of E_2:

$$P(E_2) = \left|\frac{-i}{\sqrt{6}}\right|^2 = \frac{1}{6}$$

2.31

For every observable, we define an operator
Mechanical quantities describing a particle (its energy, position vectors, momentum, angular momentum, etc.) are represented by *linear Hermitian operators* acting in the space of wave functions.
Such an operator satisfies the following conditions:

$$\hat{A}(c_1\Psi_1 + c_2\Psi_2) = c_1\hat{A}\Psi_1 + c_2\hat{A}\Psi_2$$

where c_1 and c_2 are arbitrary complex numbers and

$$\int_\tau \psi^* \hat{A}\phi \, d\tau = \int_\tau [\hat{A}\psi]^* \phi \, d\tau$$

which ensures that their eigenvalues are always real.

2.32

Another important feature of Hermitian operators
Distinct eigenvalues of a Hermitian operator correspond to orthogonal eigenfunctions. Even if more than one eigenfunction corresponds to a single eigenvalue, their linear combination is also an eigenfunction, and as a result, *one can always construct an orthogonal set of eigenfunctions of a Hermitian operator*. Hence, if the eigenvalues a_k are discrete, the corresponding eigenfunctions form an orthonormal set:

$$\int_\tau \phi_k^*(\vec{r})\phi_l(\vec{r}) \, d\tau = \delta_{kl} = \begin{cases} 1, & \text{if} \quad k = l, \\ 0, & \text{if} \quad k \neq l. \end{cases}$$

2.33

It is easy to check that this is indeed the case
If $\hat{A}$ is a Hermitian operator, then

$$\int \phi_k^* \hat{A}\phi_l \, d\tau - \int [\hat{A}\phi_k]^* \phi_l \, d\tau = 0$$

However, by assumption, we are considering the operator's eigenfunctions, so

$$\hat{A}\phi_k = a_k\phi_k$$
$$\hat{A}\phi_l = a_l\phi_l$$

and thus

$$(a_l - a_k^*) \int \phi_k^* \phi_l \, d\tau = 0$$

2.34

Operators as a linear transformation
Operators represent mechanical observables, and their action on a state vector $|\psi\rangle$ should return a number. In linear algebra this corresponds to a linear map from a vector space to a scalar (a so-called linear functional):

$$L\vec{v} \to c$$

Example in $\mathbb{R}^2$

Consider the transformation L_x, which acting on a vector returns its x-component:

$$L_x \begin{bmatrix} -1 \\ 3 \end{bmatrix} = -1$$

What is the matrix representation of L_x? It is easy to check that it is the vector $\begin{bmatrix} 1 & 0 \end{bmatrix}$:

$$\begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} -1 \\ 3 \end{bmatrix} = -1$$

2.35

Linear functionals also form a vector space (the so-called dual space). For a given vector space V, V^* is the vector space of all linear functionals

$$V^* = \{ L : V \to \mathbb{F}, \quad \mathbb{F} = \mathbb{R} \text{ or } \mathbb{C} \}$$

$$\begin{bmatrix} a \\ b \end{bmatrix} \rightsquigarrow \begin{bmatrix} a & b \end{bmatrix}$$

Returning to the example in $\mathbb{R}^2$:

$$\begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 1 \cdot a + 0 \cdot b$$

but also

$$\begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 1 \cdot a + 0 \cdot b = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \cdot \begin{bmatrix} a \\ b \end{bmatrix}$$

2.36

Thus, the action of a linear functional L_ϕ is equivalent to taking the inner product with some vector $\vec{\phi}$ (this is not a coincidence but essentially the content of the Riesz representation theorem):

$$L_\phi \vec{\psi} = \langle \phi | \psi \rangle$$

Let us return to the example of a vector given as a linear combination of orthonormal state vectors $|\psi\rangle = \sum_i c_i |E_i\rangle$, where the coefficients c_i can be obtained from the inner product $c_i = \langle E_i | \psi \rangle$. Substituting them into the equation:

$$\begin{aligned} |\psi\rangle = \sum_i \underbrace{c_i}_{\langle E_i | \psi \rangle} |E_i\rangle = \sum_i \langle E_i | \psi \rangle |E_i\rangle = \\ \sum_i |E_i\rangle \langle E_i | \psi \rangle = \underbrace{\left(\sum_i |E_i\rangle \langle E_i| \right)}_{\vec{I}} |\psi\rangle \end{aligned}$$

2.37

Example
Show that:

$$\sum_i |E_i\rangle\langle E_i| = \hat{I}$$

Apply the operator to an arbitrary state:

$$\sum_i |E_i\rangle\langle E_i|\psi\rangle = \sum_i |E_i\rangle c_i = |\psi\rangle$$

The operator acts as the identity.

2.38

Hermitian and Unitary Operators

- **Hermitian** ($A^\dagger = A$): real eigenvalues, orthonormal basis of eigenvectors (spectral theorem).
- **Unitary** ($U^\dagger U = I$): preserves inner products and norms.
- In quantum mechanics: observables $\leftrightarrow$ Hermitian operators, evolution and change of basis $\leftrightarrow$ unitary operators.

2.39

The product of operators is not always commutative
A significant property of operators is that their products may not be commutative: for two operators $\hat{A}$ and $\hat{B}$, it may happen that:

$$[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$$

Example
Let's verify this for the position and momentum operators. For simplicity, we will calculate the commutator $[\hat{x},\hat{p}_x]$.

$$\begin{aligned}[\hat{x},\hat{p}_x] &= -x\,i\hbar\frac{\partial}{\partial x}\phi(x) + i\hbar\frac{\partial}{\partial x}\big(x\phi(x)\big) \\ &= i\hbar\Big(-x\frac{\partial\phi(x)}{\partial x} + \phi(x) + x\frac{\partial\phi(x)}{\partial x}\Big) \\ &= i\hbar\end{aligned}$$

2.40

Useful commutation relations:
For operators A, B and C, the following hold:

$$[A,A] = 0$$

$$[A,B] + [B,A] = 0$$

$$[A,B+C] = [A,B] + [A,C]$$

$$[A+B,C] = [A,C] + [B,C]$$

$$[A,BC] = [A,B]C + B[A,C]$$

$$[AB,C] = [A,C]B + A[B,C]$$

2.41

Example. Evaluate the commutators:

- $[x^2, p_x] = 2i\hbar x$
- $[x^n, p_x] = ni\hbar x^{n-1}$
- $[l_x, l_y] = y[p_z, z]p_x + p_y[z, p_z]x = i\hbar l_z$
- $[x, p_x^2] = [x, p_x]p_x - p_x[p_x, x] = 2i\hbar p_x$
- $[H, p_x] = [\frac{p_x^2}{2m} + v(x), p_x] = [v(x), p_x] = i\hbar\frac{\partial v(x)}{\partial x}$

2.42

Rules for constructing operators

Observables are represented by operators that satisfy the following commutation relations:

$[q, p_{q'}] = i\hbar\delta_{qq'} \quad [q, q'] = 0 \quad [p_q, p_{q'}] = 0$

where $q \in \{x, y, z\}$ denotes the position coordinates and p_q the canonically conjugate momentum components.

2.43

Rules for constructing operators in the position representation

Mechanical quantity	Corresponding operator
x	$\hat{x} = x\cdot$
p_x	$\hat{p}_x = -i\hbar\dfrac{\partial}{\partial x}$
$p = mv$	$\hat{p} = -i\hbar\nabla = -i\hbar\Big(\dfrac{\partial}{\partial x} + \dfrac{\partial}{\partial y} + \dfrac{\partial}{\partial z}\Big)$
$T = \dfrac{mv^2}{2} = \dfrac{p^2}{2m}$	$\hat{T} = \dfrac{\hat{p}^2}{2m} = -\dfrac{\hbar^2}{2m}\nabla^2$ $= -\dfrac{\hbar^2}{2m}\Big(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\Big)$
$V(x)$	$\hat{V}(x) = V(x)\cdot$
$E = T + V$	$\hat{H} = \hat{T} + \hat{V}$

2.44

Time evolution of the particle's state

The time evolution of the state of a system described by the wave function $\Psi(\vec{r}, t)$ is governed by the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi(\vec{r}, t)}{\partial t} = \hat{H}\Psi(\vec{r}, t)$$

Knowing $\Psi(\vec{r},t_0)$ allows one to determine it at t_0+dt

$$\Psi(\vec{r},t_0+dt)=\Psi(\vec{r},t_0)-\frac{i}{\hbar}\hat{H}\Psi\,dt$$

2.45

Ideal measurement of a mechanical quantity

The outcome of a single measurement of the mechanical quantity A can only be some eigenvalue a_k of the operator $\hat{A}$, corresponding to the eigenfunction $\phi_k=\phi_k(r)$ (time-independent) satisfying:

$$\hat{A}\phi_k=a_k\phi_k \quad k=1,2,\ldots,M$$

The operator may have infinitely many eigenvalues.

2.46

Measurement outcome of a mechanical quantity

If the operators $\hat{H}$ and $\hat{A}$ commute, i.e. $[\hat{H},\hat{A}]=0$, then a *common* set of eigenfunctions of these operators can be found:

$$\left.\begin{array}{l}\hat{H}\psi_n=E_n\psi_n\\ \hat{A}\phi_k=a_k\phi_k\end{array}\right\} \quad\rightsquigarrow\quad \left.\begin{array}{l}\hat{H}\psi_{nk}=E_n\psi_{nk}\\ \hat{A}\psi_{nk}=a_k\psi_{nk}\end{array}\right\}$$

It is postulated that in the stationary state of energy E_n, described by the wave function ψ_{nk}, the measurement outcome of the mechanical quantity A must always yield the value equal to the eigenvalue a_k. Furthermore, if two operators representing mechanical quantities commute, then those quantities can be measured simultaneously with arbitrary precision.

2.47

Example

If we assume simultaneous precise measurability of the quantities A and B, then there exists a complete common set of eigenfunctions of these operators:

$$\hat{A}\psi_k=a_k\psi_k$$
$$\hat{B}\psi_k=b_k\psi_k$$

consider any linear combination of these eigenfunctions $\Psi=\sum_k c_k\psi_k$

$$\begin{aligned}[\hat{A},\hat{B}]\Psi&=(\hat{A}\hat{B}-\hat{B}\hat{A})\sum_k c_k\psi_k=\\&=\sum_k c_k(\hat{A}\hat{B}-\hat{B}\hat{A})\psi_k=\\&=\sum_k c_k(\hat{A}b_k-\hat{B}a_k)\psi_k=\\&=\sum_k c_k(a_kb_k-b_ka_k)\psi_k=0\end{aligned}$$

2.48

Generalized Heisenberg principle, Schwarz inequality
If the study of simultaneous precise measurability of two physical quantities reduces to investigating the relevant commutator, then if ΔA and ΔB denote the average standard deviations of the quantities A and B ($\Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2}$), one can prove that

$$\Delta A \Delta B \geq \frac{1}{2}\left|\langle[\hat{A},\hat{B}]\rangle\right|$$

2.49

But if they do not commute ...
If $\hat{H}$ and $\hat{A}$ do not commute, that is $[\hat{H},\hat{A}] \neq 0$, then the function ψ_n will generally not be equal to any eigenfunction of $\hat{A}$, but it can be expanded as:

$$\psi_n = \sum_{k=1}^{M} c_k \phi_k$$

Since the functions ϕ_k must be orthonormal and ψ_n must be normalized, the coefficients c_k must satisfy:

$$\sum_{k=1}^{M} c_k^* c_k = 1$$

2.50

But there is hope (mathematical) . . .
It is postulated that if the wave function ψ_n has the form

$$\psi_n = \sum_{k=1}^{M} c_k \phi_k$$

then the outcome of a single measurement of the quantity A cannot be predicted, and immediately after the measurement the wave function collapses to the eigenfunction corresponding to the measured eigenvalue ...
On the other hand, one can determine its average (expected) value:

$$\overline{a} = \frac{\int \psi_n^* \hat{A} \psi_n \, d\tau}{\int \psi_n^* \psi_n \, d\tau} = \sum_{k=1}^{M} c_k^* c_k a_k$$

2.51

Example

The state vector is given as a superposition:

$$|\psi\rangle = \sum_n c_n |E_n\rangle$$

Show that:

$$\langle H\rangle = \sum_n |c_n|^2 E_n$$

Solution:

$$\langle H\rangle = \langle\psi|\hat{H}|\psi\rangle = \sum_{mn} c_m^* c_n \langle E_m|\hat{H}|E_n\rangle = \sum_{mn} c_m^* c_n E_n \delta_{mn}$$
$$= \sum_n |c_n|^2 E_n$$

2.52

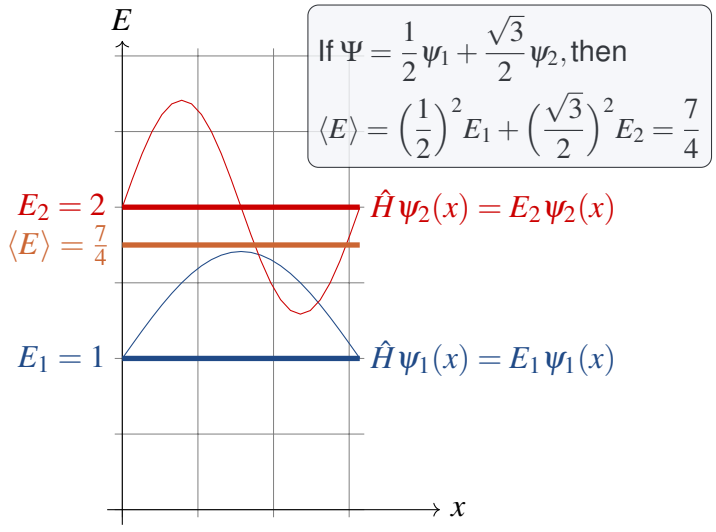
If our observable depends only on position ...

... then the expression for the average value is identical to that in classical physics. If we divide the entire space into infinitely many volume elements $d\tau$, the average value will be equal to the sum of the function's value at point P times the probability of encountering the particle at that point.

$$\overline{f} = \frac{\int f(P)\psi_n^*(P)\psi_n(P)\,d\tau}{\int \psi_n(P)^*\psi_n(P)\,d\tau}$$

2.53

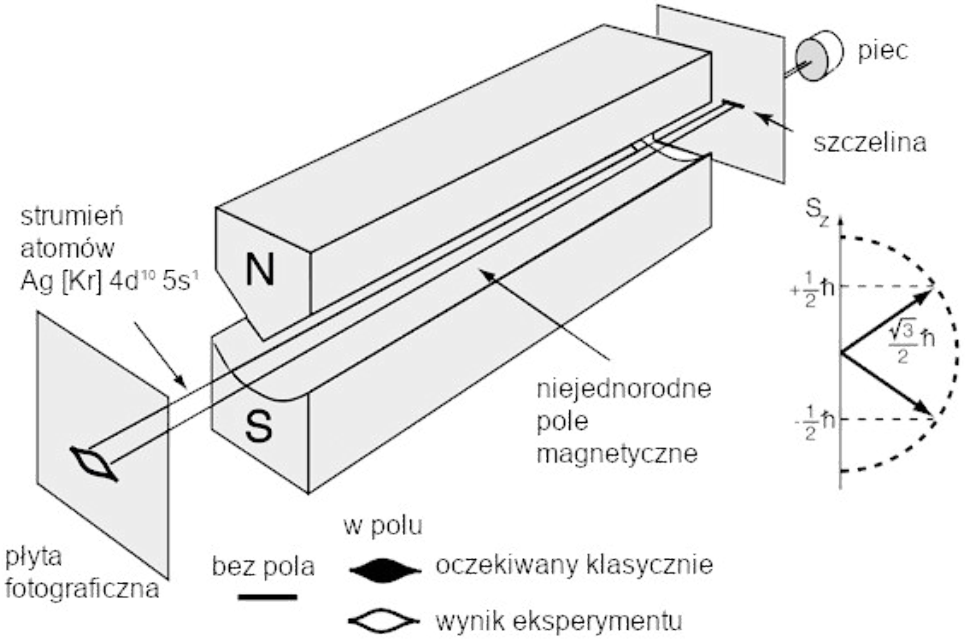
An example measurement of energy



2.54

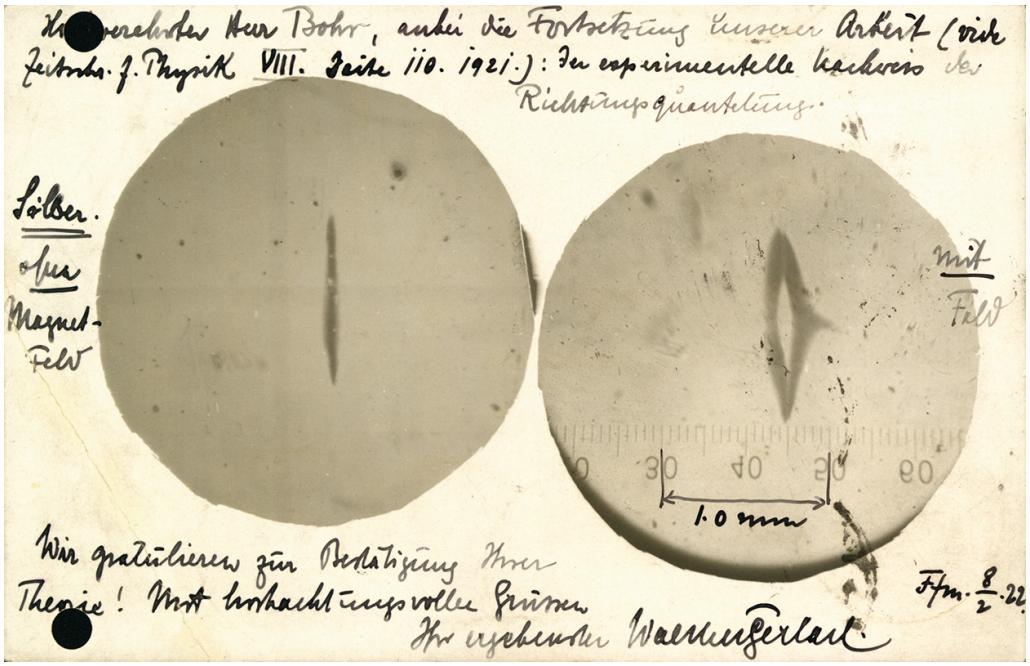
2.2 Spin

Stern-Gerlach experiment



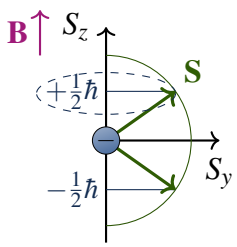
2.55

Postcard from Gerlach to Bohr



2.56

Spin and the Pauli exclusion principle



The set of quantum numbers $\{n,l,m\}$ discussed so far does not allow for a complete explanation of recorded atomic spectra. A full interpretation requires the assumption that the electron also has an intrinsic angular momentum corresponding to the quantum number $s=\frac{1}{2}$, giving a total angular momentum:

$$S=\hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}=\frac{\sqrt{3}}{2}\hbar,$$

whose projection onto a distinguished axis can take on two values:

$$S_z=\pm\frac{1}{2}\hbar.$$

2.57

In 1925, Wolfgang Pauli, based on an analysis of alkali metal atom spectra, concluded that two electrons cannot occupy the same quantum state. This leads to the simple conclusion that the wave function of electrons (and in fact of all fermions) must be antisymmetric:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)=-\Psi(\mathbf{x}_2,\mathbf{x}_1,\ldots,\mathbf{x}_N)$$

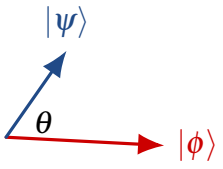
because such a wave function must be zero when two “identical” electrons coincide:

$$\Psi(\mathbf{x}_1,\mathbf{x}_1,\ldots,\mathbf{x}_N)=-\Psi(\mathbf{x}_1,\mathbf{x}_1,\ldots,\mathbf{x}_N)=0$$

2.58

2.3 Unitary operators

Unitary transformation



Can there be an operator that preserves the inner product of two state vectors?

$$\langle\psi|\phi\rangle \stackrel{?}{=} \langle\hat{U}\psi|\hat{U}\phi\rangle$$

Yes. For example, for two vectors, a rotation preserves the lengths and the angle between them, and therefore also the scalar product.

$$|\psi||\phi|\cos(\theta) = |\hat{U}\psi||\hat{U}\phi|\cos(\theta_U)$$

In general, operators that preserve the inner product $\langle\psi|\phi\rangle$ are called unitary operators (whose *Hermitian conjugate equals their inverse*):

$$\hat{U}^\dagger = \hat{U}^{-1}.$$

Unitary operators represent *generalized rotations*.

2.59

The condition $\hat{U}^\dagger = \hat{U}^{-1}$ preserves the inner product

$$\langle\psi|\phi\rangle \stackrel{?}{=} \langle\hat{U}\psi|\hat{U}|\phi\rangle = \langle\psi|\hat{U}^\dagger\hat{U}|\phi\rangle = \langle\psi|\hat{U}^{-1}\hat{U}|\phi\rangle = \langle\psi|\hat{I}|\phi\rangle$$
$$\langle\hat{U}\psi|\hat{U}|\phi\rangle = \langle\psi|\phi\rangle$$

Consider the following eigenvalue problem

$$\hat{U}|\omega\rangle = \lambda|\omega\rangle$$

where $\langle\omega|\omega\rangle = 1$. Apply $\hat{U}$ to this inner product:

$$\langle\hat{U}\omega|\hat{U}\omega\rangle = \langle\lambda\omega|\lambda\omega\rangle = \lambda\lambda^*\langle\omega|\omega\rangle = |\lambda|^2 = 1$$

The eigenvalues of unitary operators have unit magnitude (hence the name "unitary"). This is natural since eigenvalues scale the length of the vector.

2.60

What do inner products represent in QM?

In quantum mechanics, the inner product of two state vectors typically represents probability:

$$|\langle E_i|\psi\rangle|^2 = P(E_i),$$

so *the action of a unitary operator on the inner product preserves probability*:

$$|\langle\hat{U}E_i|\hat{U}\psi\rangle|^2 = P(E_i), \quad \langle\hat{U}\psi|\hat{U}\psi\rangle = 1.$$

In particular, rotation operators $\hat{R}(\theta)$, translation operators $\hat{T}(\vec{a})$, and time evolution operators $\hat{U}(t)$ must be unitary to preserve probability.

2.61

2.4 Generators

What are generators in classical mechanics?

$$E \rightsquigarrow \frac{\partial}{\partial t}, \quad p \rightsquigarrow \frac{\partial}{\partial x},$$
$$x \rightsquigarrow \frac{\partial}{\partial p}, \quad L \rightsquigarrow \frac{\partial}{\partial \theta}.$$

State vector $\psi(q,t)$ in QM vs. Lagrangian $\mathscr{L}(t,x,\dot{x})$

The vector $|\psi\rangle$ represents the quantum-mechanical state of the system, including possible positions $\{x\}$, momenta $\{p\}$, energies $\{E\}$, etc.

$$|\psi\rangle$$

In Newtonian mechanics, there is no direct equivalent. The analogous role is played by the Lagrangian $\mathscr{L}$ in the Lagrangian formalism based on Hamilton's principle of stationary action:

$$\mathscr{L}.$$

2.62

The Lagrangian $\mathscr{L}(t,x,\dot{x})$

The Lagrangian $\mathscr{L}(t,x,\dot{x})$ is a function representing the state of a classical mechanical system, depending on time t, position $x(t)$, and velocity $\dot{x}(t)$ of the particles in the system, defined as the difference between their kinetic and potential energies:

$$\mathscr{L} = \frac{1}{2}m\dot{x}^2 - V(x).$$

The trajectory $x(t)$ is determined by the stationary points of the action integral:

$$S[\mathscr{L}] = \int_{t_i}^{t_f} dt\, \mathscr{L}\big(t, x(t), \dot{x}(t)\big).$$

2.63

$x(t)$ determines the action integral $S[\mathscr{L}]$

$$S[\mathcal{L}] = \int_{t_i}^{t_f} dt\ \mathcal{L}(t, x(t), \dot{x}(t)) \qquad S[\mathcal{L}] = \int_{t_i}^{t_f} dt\ \mathcal{L}(t, x(t), \dot{x}(t))$$



The function $x(t)$ for which $S[\mathscr{L}]$ is stationary satisfies the Euler-Lagrange equations:

$$\frac{\partial \mathscr{L}}{\partial x} = \frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \dot{x}},$$

and substituting $\mathscr{L} = \frac{1}{2}m\dot{x}^2 - V(x)$, we get:

$$-\frac{dV(x)}{dx} = \frac{d}{dt}(m\dot{x}) \ \rightsquigarrow\ m\ddot{x} = ma = F.$$

2.64

Interpretation of $\mathscr{L}$

Interpreting $\mathscr{L}$ as the system state, changes in the particle momenta are connected with variations of $\mathscr{L}$ with respect to positions:

$$\frac{\partial \mathscr{L}}{\partial x} = \frac{d}{dt}p.$$

Likewise, substituting $\mathscr{L} = \frac{p^2}{2m} - V(x)$, one obtains:

$$\frac{\partial \mathscr{L}}{\partial p} = \frac{p}{m} = \frac{d}{dt}x.$$

In other words, if t and x are fixed, analyzing changes in the system state $\mathscr{L}$ is equivalent to analyzing position changes over time. Spatial translations are associated with momentum.

2.65

Interpretation of $\mathscr{L}$

The interpretation of the dependence of $\mathscr{L}$ on time is somewhat more involved:

$$\begin{aligned}\frac{d}{dt}\mathscr{L}(t,x(t),\dot{x}(t)) &= \frac{\partial\mathscr{L}}{\partial t}+\frac{\partial\mathscr{L}}{\partial x}\frac{dx}{dt}+\frac{\partial\mathscr{L}}{\partial\dot{x}}\frac{d\dot{x}}{dt}\\ &= \frac{\partial\mathscr{L}}{\partial t}+\frac{\partial\mathscr{L}}{\partial x}\dot{x}+\frac{\partial\mathscr{L}}{\partial\dot{x}}\frac{d\dot{x}}{dt}\\ &= \frac{\partial\mathscr{L}}{\partial t}+\frac{d}{dt}\left(\frac{\partial\mathscr{L}}{\partial\dot{x}}\right)\dot{x}+\frac{\partial\mathscr{L}}{\partial\dot{x}}\frac{d\dot{x}}{dt}\\ &= \frac{\partial\mathscr{L}}{\partial t}+\frac{d}{dt}\left(\frac{\partial\mathscr{L}}{\partial\dot{x}}\dot{x}\right)\end{aligned}$$

$$\frac{\partial\mathscr{L}}{\partial t}+\frac{d}{dt}\left(\frac{\partial\mathscr{L}}{\partial\dot{x}}\dot{x}\right)=\frac{d}{dt}\mathscr{L}$$

$$\frac{\partial\mathscr{L}}{\partial t}=\frac{d}{dt}\left(\mathscr{L}-\frac{\partial\mathscr{L}}{\partial\dot{x}}\dot{x}\right)=\frac{d}{dt}\left(\mathscr{L}-m\dot{x}\dot{x}\right)=-\frac{d}{dt}E$$

By analogy, analyzing the state of the system through $\mathscr{L}$ for constant x and p corresponds to analyzing the time evolution of the energy E.

2.66

So what are generators in classical mechanics?

$$E\rightsquigarrow\frac{\partial}{\partial t}\quad p\rightsquigarrow\frac{\partial}{\partial x}$$
$$x\rightsquigarrow\frac{\partial}{\partial p}\quad L\rightsquigarrow\frac{\partial}{\partial\theta}$$

In other words, the dependence of $\mathscr{L}$ on some physical parameter is equivalent to the time evolution of the conjugate parameter. Momentum generates translations, angular momentum generates rotations, and energy (the Hamiltonian) is the generator of time evolution, etc.

$$\frac{\partial\mathscr{L}}{\partial x}=\frac{d}{dt}p\qquad\frac{\partial\mathscr{L}}{\partial p}=\frac{d}{dt}x$$
$$\frac{\partial\mathscr{L}}{\partial t}=-\frac{d}{dt}E\quad\frac{\partial\mathscr{L}}{\partial\theta}=\frac{d}{dt}L$$

If $\mathscr{L}\iff|\psi\rangle$, then intuitively the energy operator generates the time evolution of the state of the system:

$$\frac{d}{dt}|\psi\rangle\rightsquigarrow\hat{E}$$

2.67

2.5 Schrödinger Equation

Time-evolution operator $\hat{U}(t)$
In classical mechanics, energy generates the time evolution of a system:

$$\frac{\partial \mathscr{L}}{\partial t} = -\frac{d}{dt}E$$

To describe the time evolution of the quantum-mechanical state of a system $|\psi(t)\rangle$, it is necessary to introduce an appropriate operator — the time-evolution operator $\hat{U}(t)$, which propagates the state vector in time:

$$\hat{U}(2fs)|\psi\rangle = |\psi(2fs)\rangle$$

2.68

Time-evolution operator $\hat{U}(t)$
What properties should $\hat{U}(t)$ have?

- $\hat{U}(0)$ should return the unchanged state $|\psi\rangle$

$$\hat{U}(0)|\psi\rangle = |\psi\rangle \rightsquigarrow \hat{U}(0) = \hat{I}$$

- Time evolution is reversible, therefore $\hat{U}^{-1}(t)$ must exist
- Propagation of the state vector should preserve the probabilistic interpretation (i.e., conserve total probability)

$$\langle \hat{U}(t)\psi|\hat{U}(t)\psi\rangle = \langle\psi|\psi\rangle = 1$$

This is a property of unitary operators!

2.69

The time-evolution operator $\hat{U}(t)$ ***is unitary***
Propagation of the state vector should preserve the probabilistic interpretation (i.e., conserve total probability)

$$\langle \hat{U}(t)\psi|\hat{U}(t)\psi\rangle = \langle\psi|\psi\rangle = 1$$

This is a property of unitary operators!

$$\begin{aligned}
\langle \hat{U}\psi|\hat{U}|\psi\rangle = \langle\psi|\hat{U}^\dagger\hat{U}|\psi\rangle &= \langle\psi|\psi\rangle \\
\langle\psi|\hat{U}^\dagger\hat{U}|\psi\rangle &= \langle\psi|\hat{I}|\psi\rangle \\
\langle\psi|\hat{U}^\dagger\hat{U}|\psi\rangle - \langle\psi|\hat{I}|\psi\rangle &= 0 \\
\langle\psi|\hat{U}^\dagger\hat{U} - \hat{I}|\psi\rangle &= 0
\end{aligned}$$

One can show that the operator $\hat{U}^\dagger\hat{U} - \hat{I}$ is Hermitian:[a]

$$(\hat{U}^\dagger\hat{U} - \hat{I})^\dagger = (\hat{U}^\dagger\hat{U})^\dagger - \hat{I}^\dagger = \hat{U}^\dagger\hat{U} - \hat{I}$$

[a] the Hermitian conjugate of a product reverses the order and distributes the conjugation

2.70

The time-evolution operator $\hat{U}(t)$ is unitary

Since the operator $\hat{U}^\dagger\hat{U} - \hat{I}$, call it $\hat{A}$, is Hermitian, it has an orthonormal eigenbasis $\{|a_i\rangle\}$

$$\begin{aligned}\langle\psi|\hat{U}^\dagger\hat{U} - \hat{I}|\psi\rangle &= 0\\ \langle\psi|\hat{A}|\psi\rangle &= 0\end{aligned}$$

This equation must hold for any state, and therefore also for any $|a_i\rangle$, where $\hat{A}|a_i\rangle = \lambda_i|a_i\rangle$

$$\langle a_i|\hat{A}|a_i\rangle = 0 \rightsquigarrow \langle a_i|\lambda_i|a_i\rangle = 0 \rightsquigarrow \lambda_i\langle a_i|a_i\rangle = 0 \rightsquigarrow \lambda_i = 0$$

The eigenvalues of $\hat{A}$ are equal to 0! Thus, acting on any state vector $|\psi\rangle$

$$\hat{A}|\psi\rangle = \hat{A}\sum_i c_i|a_i\rangle = \sum_i c_i\hat{A}|a_i\rangle = \sum_i c_i 0|a_i\rangle = 0$$

Therefore:

$$\hat{A} = \hat{U}^\dagger\hat{U} - \hat{I} = 0 \rightsquigarrow \hat{U}^\dagger\hat{U} = \hat{I} \rightsquigarrow \hat{U}^\dagger\hat{U}\hat{U}^{-1} = \hat{I}\hat{U}^{-1} \rightsquigarrow \hat{U}^\dagger = \hat{U}^{-1}$$

2.71

Action of the operator $\hat{U}(t)$

Let us consider the action of the operator $\hat{U}(t)$ for an infinitesimally small time change dt. This allows us to expand the operator in a Taylor series:

$$\begin{aligned}\hat{U}(dt) &= \hat{U}(0) + \dot{\hat{U}}(0)dt + \hat{\mathscr{O}}(dt^2)\\ \hat{U}(dt) &= \hat{I} + \dot{\hat{U}}(0)dt + \hat{\mathscr{O}}(dt^2)\\ \hat{U}(dt)|\psi\rangle &= |\psi\rangle + \dot{\hat{U}}(0)dt|\psi\rangle + \hat{\mathscr{O}}(dt^2)|\psi\rangle\\ |\psi(dt)\rangle &= |\psi\rangle + \dot{\hat{U}}(0)dt|\psi\rangle + \hat{\mathscr{O}}(dt^2)|\psi\rangle\\ |\psi(dt)\rangle - |\psi\rangle &= \dot{\hat{U}}(0)dt|\psi\rangle + \hat{\mathscr{O}}(dt^2)|\psi\rangle\\ \frac{|\psi(dt)\rangle - |\psi\rangle}{dt} &= \dot{\hat{U}}(0)|\psi\rangle + \frac{\hat{\mathscr{O}}(dt^2)}{dt}|\psi\rangle\\ \lim_{dt\to 0}\frac{|\psi(dt)\rangle - |\psi\rangle}{dt} &= \dot{\hat{U}}(0)|\psi\rangle + \lim_{dt\to 0}\frac{\hat{\mathscr{O}}(dt^2)}{dt}|\psi\rangle\\ \frac{d}{dt}|\psi\rangle &= \dot{\hat{U}}(0)|\psi\rangle\end{aligned}$$

2.72

Action of the operator $\hat{U}(t)$

We have not yet used the unitarity of the time-evolution operator. Let us first consider the unitarity of the Taylor expansion:

$$\begin{aligned}
\hat{I} &= \hat{U}^{-1}(dt)\hat{U}(dt) = \hat{U}^{\dagger}(dt)\hat{U}(dt) \\
\hat{I} &= \left(\hat{I} + \dot{\hat{U}}^{\dagger}(0)dt + \hat{\mathscr{O}}(dt^2)^{\dagger}\right)\left(\hat{I} + \dot{\hat{U}}(0)dt + \hat{\mathscr{O}}(dt^2)\right) \\
\hat{I} &= \hat{I} + \dot{\hat{U}}^{\dagger}(0)dt + \dot{\hat{U}}(0)dt + \hat{\mathscr{O}}(dt^2) \\
0 &= \dot{\hat{U}}^{\dagger}(0) + \dot{\hat{U}}(0) + \frac{\hat{\mathscr{O}}(dt^2)}{dt} \\
\dot{\hat{U}}^{\dagger}(0) &= -\dot{\hat{U}}(0)
\end{aligned}$$

Thus the time-evolution operator is anti-Hermitian! It is easy to check that multiplying such an operator by the imaginary unit i gives a Hermitian operator:

$$(i\dot{\hat{U}}(0))^{\dagger} = \dot{\hat{U}}^{\dagger}(0)i^{\dagger} = i\dot{\hat{U}}(0) = \hat{H} \tag{2.73}$$

Action of the operator $\hat{U}(t)$

Returning to the derived differential equation we obtain:

$$\begin{aligned}
\frac{d}{dt}|\psi\rangle &= \dot{\hat{U}}(0)|\psi\rangle \\
\frac{d}{dt}|\psi\rangle &= \left(\frac{\hat{H}}{i}\right)|\psi\rangle \\
i\frac{d}{dt}|\psi\rangle &= \hat{H}|\psi\rangle
\end{aligned} \tag{2.74}$$

Time evolution of the state vector

Assuming only reversibility of time evolution and conservation of total probability, we obtained an almost complete Schrödinger equation — the time evolution of the state vector equals the action of some Hermitian operator on that vector:

$$i\frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle$$

To determine what physical quantity the operator $\hat{H}$ represents, we must refer to the physical intuition from classical mechanics in the Lagrangian formulation:

$$\frac{\partial \mathscr{L}}{\partial t} = -\frac{d}{dt}E$$

In classical mechanics, energy generates the time evolution of the system, therefore $\hat{H}$ is the Hamiltonian. It remains to introduce the constant ensuring the correct units:

$$i\hbar\frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle$$

2.75

2.6 Free Particle

A free particle in one-dimensional space
Let us consider a particle moving freely in an unbounded one-dimensional region in a constant (and therefore also zero) potential. The Hamiltonian of the particle can then be written as:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

and the Schrödinger equation

$$\frac{d^2}{dx^2}\Psi_n(x) = -\frac{2mE_n}{\hbar^2}\Psi_n(x)$$

2.76

A linear second-order differential equation
A simple example of such an equation is:

$$\frac{d^2y}{dx^2} + k^2 y = 0$$

To solve it, we assume that $y = \exp(lx)$, which upon substitution leads to

$$(l^2 + k^2)y = 0$$

that is, $l = \pm ik$ and $y = \exp(\pm ikx)$. Thus we have two independent solutions, and since our differential equation is linear, their linear combination is also a solution:

$$y = Ae^{ikx} + Be^{-ikx} \quad \text{or, using Euler's formula}$$
$$y = C\cos kx + D\sin kx$$

2.77

Returning to our equation . . .

$$\frac{d^2}{dx^2}\Psi_n(x) = -\frac{2mE_n}{\hbar^2}\Psi_n(x)$$

its solution is the wavefunction

$$\Psi_n(x) = Ae^{ik_n x} + Be^{-ik_n x}$$

where $k_n^2 = \frac{2mE_n}{\hbar^2}$. Since there are no boundary conditions, there are no restrictions on the values of E_n.

2.78

Example

To understand the meaning of the coefficients A and B, let us determine the eigenvalues of the momentum operator by setting them equal to zero one at a time:

If $B = 0$

$$\hat{p}\Psi_n(x) = \frac{\hbar}{i}\frac{d\Psi_n(x)}{dx} = \frac{\hbar}{i}\frac{d}{dx}Ae^{ik_n x} = k_n\hbar Ae^{ik_n x} = k_n\hbar\Psi_n(x)$$

If $A = 0$

$$\hat{p}\Psi_n(x) = \frac{\hbar}{i}\frac{d\Psi_n(x)}{dx} = \frac{\hbar}{i}\frac{d}{dx}Be^{-ik_n x} = -k_n\hbar Be^{-ik_n x} = -k_n\hbar\Psi_n(x)$$

As we can see, the wavefunction $\Psi_n(x)$ is a superposition of two eigenfunctions of the momentum operator corresponding to a particle moving with the same speed in the positive or negative x direction.

2.79

The state of a free particle is described by a wave packet

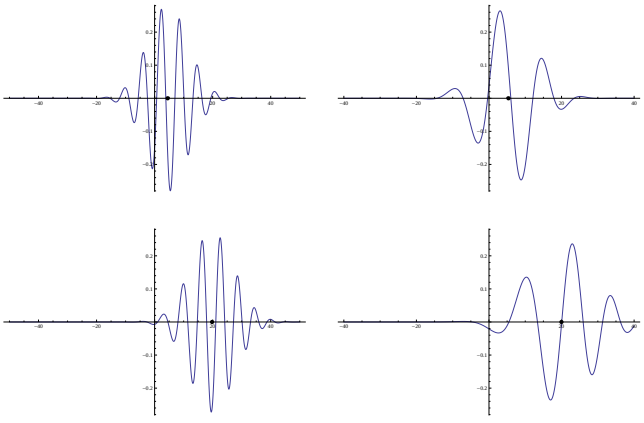
If the energy (or momentum) of the free particle is not known exactly, or if we try to measure it, the state of the particle will no longer be described by a monochromatic wave but rather by a superposition of many different waves

$$\Psi = \sum_n c_n\psi_n$$

Such a packet will be localized in space because everywhere outside a small region (whose center moves with the average velocity $< p > /m$) the waves ψ_n will cancel due to interference.

2.80

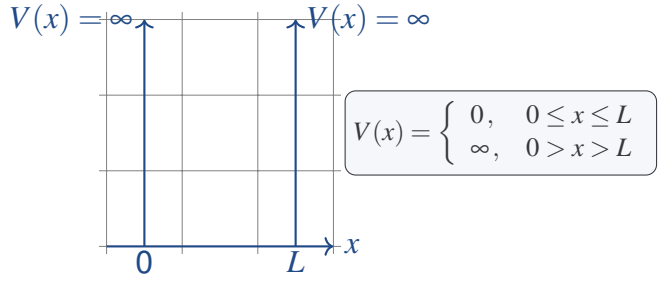
$< p >= 1$ $< p >= 0.5$



2.81

2.7 Particle in a Potential Box

One of the simplest cases for which the Schrödinger equation can be solved analytically is a particle in an infinite one-dimensional rectangular potential box.



2.82

Schrödinger equation for a particle in an infinite potential well
It is essentially identical to that for a free particle . . .

$$\frac{d^2}{dx^2}\Psi_n(x) = -\frac{2mE_n}{\hbar^2}\Psi_n(x)$$

this time, however, the wavefunction must satisfy certain boundary conditions — in particular, it must vanish exponentially over an infinitesimally small distance at the boundaries of the well.

2.83

Schrödinger equation for a particle in an infinite potential well
A simple explanation is obtained by writing the Schrödinger equation for regions with infinite potential:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi_n(x) = (E-\infty)\Psi_n(x)$$

Therefore, if $\Psi_n(x)$ is a function of class Q, the derivative on the left-hand side must be finite, and then $\Psi_n(x) = 0$

2.84

If the differential equations are the same . . .
. . . then the solutions should also be the same:

$$\begin{aligned}\Psi_n(x) &= A\exp\left(i\frac{p_n}{\hbar}x\right) + B\exp\left(-i\frac{p_n}{\hbar}x\right) \\ &= C\cos\left(\frac{p_n x}{\hbar}\right) + D\sin\left(\frac{p_n x}{\hbar}\right)\end{aligned}$$

. . . only the boundary conditions change:
$\Psi_n(0) = 0$ and therefore $C = 0$
$\Psi_n(L) = D\sin\left(\frac{p_n L}{\hbar}\right) = 0$ and therefore $p_n = \frac{n\pi\hbar}{L}$

$$\Psi_n(x) = D\sin\left(\frac{n\pi}{L}x\right)$$

2.85

The constant D is found from the normalization condition

$$1 = \int_0^L \psi^* \psi \, dx = \int_0^L D^2 \sin^2\left(\frac{\pi x}{L}\right) dx = \frac{1}{2} L D^2$$

$$\rightsquigarrow \quad \psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

To find the energy, it is enough to substitute our wavefunction into the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) = E\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

$$E = \frac{(n\pi\hbar)^2}{2mL^2} = \frac{n^2 h^2}{8mL^2}$$

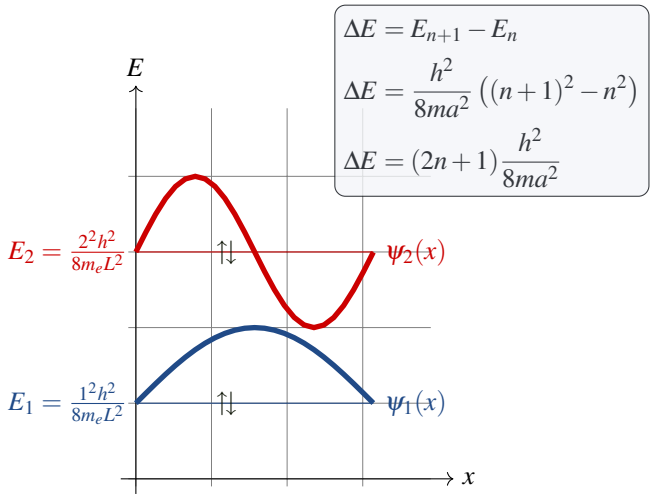
2.86

Conclusions?

- Energy can take only discrete values (they become more densely spaced the stronger the potential localizing the particle and the wider the potential well)
- the kinetic energy of a particle confined to any region of space cannot be equal to zero

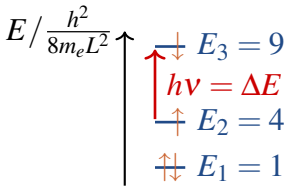
2.87

Simple applications - FEMO



2.88

Example: the butadiene molecule

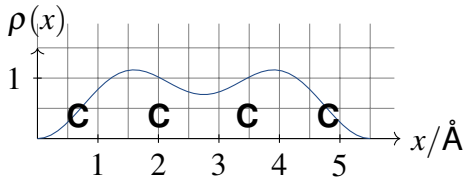


We estimate the maximum of the absorption band for the $\pi \rightarrow \pi^*$ transition in the butadiene molecule $CH_2{=}CH{-}CH{=}CH_2$, assuming that $R_{C-C} = 1.46$Å and $R_{C=C} = 1.34$Å. We estimate the width of the box as the sum of the bond lengths, adding half a bond at each end: $L = 5.48$Å. Since we have 4 π electrons, the lowest excitation energy is:

$$\Delta E = E_3 - E_2 = (5)\frac{h^2}{8ma^2} = h\nu = \frac{hc}{\lambda}$$

The wavelength determined in this way corresponding to the absorption maximum is $198.1\,nm$, already close to the experimentally observed value of $210.0\,nm$. Treating the electrons in this model as independent particles, we find the electron density distribution $\rho(x)$ in the ground state as:

$$\rho(x) = 2\psi_1^2 + 2\psi_2^2 = \frac{4}{L}\left[\sin^2\left(\frac{\pi}{L}x\right) + \sin^2\left(\frac{2\pi}{L}x\right)\right]$$



2.89

Particle in a periodic box

By slightly modifying the boundary conditions of the solutions for a particle in a one-dimensional potential box, one can attempt to describe the benzene molecule within the FEMO approximation. This time we would like, in a sense, to "stitch" the two ends of the potential well together, thereby introducing *periodic boundary conditions*. The conditions that our function must satisfy are:

$$\left.\begin{aligned}\psi_n(0) &= \psi_n(L)\\ \psi_n'(0) &= \psi_n'(L)\end{aligned}\right\} \rightsquigarrow$$

$$\left.\begin{aligned}A\sin k0 + B\cos k0 &= A\sin kL + B\cos kL\\ Ak\cos k0 - Bk\sin k0 &= Ak\cos kL - Bk\sin kL\end{aligned}\right\}$$

$$\left.\begin{aligned}A\sin kL + B(\cos kL - 1) &= 0\\ A(\cos kL - 1) - B\sin kL &= 0\end{aligned}\right\} \rightsquigarrow \begin{vmatrix}\sin kL & (\cos kL - 1)\\ (\cos kL - 1) & -\sin kL\end{vmatrix} = 0$$

which leads to:

$$\cos kL = 1 \rightsquigarrow kL = 2n\pi \quad \text{for} \quad n = 0, \pm 1, \pm 2, \ldots \quad E_n = \frac{(2n)^2h^2}{8mL^2}$$

2.90

Particle in a periodic box

The general form of the wavefunction is $\psi_n = A\sin\frac{2n\pi x}{L} + B\cos\frac{2n\pi x}{L}$.

$$\psi_0 = B \rightsquigarrow \psi_0 = \sqrt{\frac{1}{L}} \text{ since } B^2\int_0^L dx = 1.$$

Next, using the odd/even parity of the (sin)cos functions, we can write:

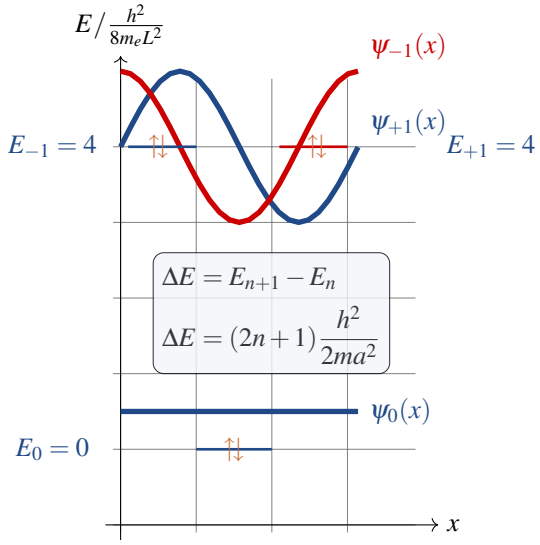
$$\psi_{n>0} = A\sin\frac{2n\pi x}{L} + B\cos\frac{2n\pi x}{L}$$
$$\psi_{n<0} = -A\sin\frac{2|n|\pi x}{L} + B\cos\frac{2|n|\pi x}{L}$$

Since for any n both functions have the same energy eigenvalue, we may take any normalized linear combination of them, for example by adding and subtracting them, which leads (after determining the constants A and B) to:

$$\Psi_0 = \sqrt{\frac{1}{L}} \qquad \Psi_{n>0} = \sqrt{\frac{2}{L}}\sin\frac{2n\pi x}{L} \quad \text{for } n > 0$$
$$\Psi_{n<0} = \sqrt{\frac{2}{L}}\cos\frac{2n\pi x}{L} \quad \text{for } n < 0$$

2.91

Particle in a periodic box

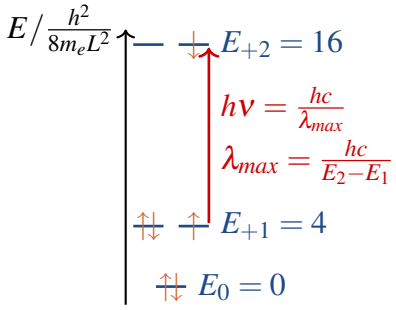


2.92

Example

Calculate the wavelengths corresponding to the absorption maximum for the $\pi \rightarrow \pi^*$ transition in the benzene molecule within the FEMO approximation.

Energy diagram



The "width" of the well is equal to the length of 6 bonds!

$$L = 6 \cdot 1.4 \cdot 10^{-10}\, m$$

$$\Delta E = \frac{(4^2 - 2^2)h^2}{8m_eL^2} = \frac{hc}{\lambda_{max}}$$

$$\lambda_{max} = \frac{8m_ecL^2}{12h} = 194\, nm$$

The experimental value of the ${}^1\pi\pi^*$ absorption-band maximum is about $178\, nm$. It is worth emphasizing that in cyclic systems the width of the well is equal to the sum of the bond lengths, unlike in quasi-linear polyenes, where we added half a bond at each end.

2.93

Chapter 3
Electronic and vibrational molecular states

3.94

3.1 Time-(in)dependent Schrödinger equation

Time evolution of a state vector
The evolution in time of a quantum mechanical system is governed by the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \hat{H}\Psi(\vec{r},t)$$

Knowing a state vector at time t_0 allows to *determine* its evolution

$$\Psi(\vec{r},t_0+dt) = \Psi(\vec{r},t_0) - \frac{i}{\hbar}\hat{H}\Psi\, dt$$

3.95

Time-independent Schrödinger equation
If Hamiltonian does not depend on time one can formally separate spatial and temporal variables:

$$\begin{aligned}
&i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \hat{H}\Psi(\vec{r},t)\\
&i\hbar\frac{\partial\psi(\vec{r})f(t)}{\partial t} = \hat{H}\psi(\vec{r})f(t) \quad \text{for}\,\hat{H}\neq\hat{H}(t)\\
&i\hbar\frac{1}{f(t)}\frac{\partial f(t)}{\partial t} = \frac{\hat{H}\psi(r)}{\psi(r)} = E
\end{aligned}$$

$$\left.\begin{aligned}\hat{H}\psi(\vec{r}) &= E\psi(\vec{r})\\ \tfrac{df(t)}{f(t)} &= -\tfrac{i}{\hbar}E dt\end{aligned}\right\}$$

$$\rightsquigarrow f(t)\propto e^{-iEt/\hbar}$$

$$\rightsquigarrow \Psi(\vec{r},t) = e^{-iEt/\hbar}\psi(\vec{r})$$

3.96

3.2 Molecular Hamiltonian

All quantum mechanical information about the stationary properties of the molecular system is contained in the solutions of the time-independent nonrelativistic Schrödinger equation

$$H_m \Psi(r,\sigma;R) = \varepsilon \Psi(r,\sigma;R)$$

For many electron system:

$$H_m = \underbrace{-\frac{1}{2}\sum_{\alpha}\frac{\nabla_\alpha^2}{M_\alpha}}_{T_n} \underbrace{-\frac{1}{2m_e}\sum_i \nabla_i^2}_{T_e} + \underbrace{\underbrace{\sum_{\alpha>\beta}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}}_{V_{nn}} \underbrace{-\sum_{\alpha,i}\frac{Z_\alpha}{R_{\alpha i}}}_{V_{en}} + \underbrace{\sum_{i>j}\frac{1}{r_{ij}}}_{V_{ee}}}_{V}$$

Since Hamiltonian does not depend on spin the solution can be separated:

$$\Psi(r,\sigma;R) = \psi(r;R)\zeta(\sigma) \text{ where } \zeta(\sigma) = (\langle\sigma_1|\langle\sigma_2|\ldots\langle\sigma_{N_e}|)\,|\zeta\rangle \tag{3.97}$$

3.3 Born–Oppenheimer Separation

Due to large mass difference the electronic degrees of freedom respond instantaneously to changes in the nuclear configuration. V_{en} is thus modified only *adiabatically* due to nuclear motion and does not cause electronic transitions.

$$H_e(R) = T_e + V_{en} + V_{ee}$$

In consequence the solutions of electronic Schrödinger equation describing the motion of the electrons in field of stationary nuclei will depend parametrically on the set of nuclear coordinates

$$H_e(R)\phi_a(r;R) = E_a(R)\phi_a(r;R)$$

Adiabatic electronic states define a complete basis set in the electronic Hilbert space in which the molecular wave function can be expanded

$$\psi(r;R) = \sum_a \chi_a(R)\phi_a(r;R) \tag{3.98}$$

Substituting expansion coefficients into Schrödinger equation leads to

$$\begin{aligned} H_m(R)\psi(r;R) &= (H_e(R)+T_n+V_{nn})\sum_a \chi_a(R)\phi_a(r;R) \\ &= \sum_a [E_a(R)+V_{nn}]\chi_a(R)\phi_a(r;R) \\ &+ \sum_a T_n\chi_a(R)\phi_a(r;R) \\ &= \varepsilon\sum_a \chi_a(R)\phi_a(r;R) \end{aligned}$$

Multiplication from left by $\phi_b^*(r;R)$ and integration over electronic coordinates yields

$$\begin{aligned} \int dr\,\phi_b^*(r;R)H_m\psi(r;R) =& [E_b(R)+V_{nn}]\chi_b(R) \\ &+ \sum_a \int dr\,\phi_b^*(r;R)T_n\phi_a(r;R)\chi_a(R) \\ &= \varepsilon\chi_b(R) \end{aligned}$$

3.99

$$\begin{aligned} T_n\phi_a(r;R)\chi_a(R) =& \sum_n \frac{1}{2M_n}\{\mathbf{P}_n^2\phi_a(r;R)\chi_a(R) \\ &+ 2[\mathbf{P}_n\phi_a(r;R)]\mathbf{P}_n\chi_a(R) \\ &+ \phi_a(r;R)\mathbf{P}_n^2\chi_a(R)\} \end{aligned}$$

The last term is simply nuclear kinetic energy and the remaining ones can be put into so-called *nonadiabacity* operator

$$\begin{aligned} \Theta_{ab} =& \int dr\,\phi_a(r;R)T_n\phi_b(r;R) \\ &+ \sum_n \frac{1}{M_n}\left[\int dr\,\phi_a(r;R)\mathbf{P}_n\phi_b(r;R)\right]\mathbf{P}_n \end{aligned}$$

3.100

In consequence we obtain an (still exact) equation for coefficients $\chi_a(R)$

$$(T_n + E_a(R) + V_{nn} + \Theta_{aa} - \varepsilon)\chi_a(R) = -\sum_{b\neq a}\Theta_{ab}\chi_b(R)$$

which can be viewed as the stationary Schrödinger equation for the nuclear motion with $\chi_a(R)$ being the respective wave functions. The solution of above equation leads to the following molecular wave function

$$\psi_M(r;R) = \sum_a \chi_{aM}(R)\phi_a(r;R)$$

where vibrational quantum number M is not related to any individual electronic state.

3.101

3.4 Potential energy surfaces

It is convenient to introduce the following effective potential for the nuclear motion in a given adiabatic state $|\phi_a\rangle$

$$U_a(R) = E_a(R) + V_{nn} + \Theta_{aa}$$

which defines a hypersurface in the space of nuclear coordinates, the so-called *potential energy surface*

3.102

3.5 Born–Oppenheimer Approximation

In practice it is often possible to neglect the nonadiabatic couplings. This leads to the following approximation

$$H_a(R)\chi_a(R) = (T_n + U_a(R))\chi_a(R) = \varepsilon\chi_a(R)$$

in which nuclei move in an effective potential $U_a(R)$ due to their mutual Coulomb interactions and interaction with electronic charge density. The resulting adiabatic wave function becomes

$$\psi_{aM}^{(adia)}(r;R) = \sum_a \chi_{aM}(R)\phi_a(r;R)$$

where the vibrational quantum number M is related to a particular electronic state. Considering perturbational expansion of the energy ε_{aM} with respect to nonadiabacity operator Θ_{ab} it is obvious that if the two adiabatic surfaces are close to each other BO approximation is no longer valid.

$$\varepsilon_{aM}^{(2)} = \varepsilon_{aM}^{(adia)} + \sum_{bN} \frac{|\langle\chi_{aM}|\Theta_{ab}|\chi_{bN}\rangle|^2}{\varepsilon_{aM}^{(adia)} - \varepsilon_{bN}^{(adia)}}$$

3.103

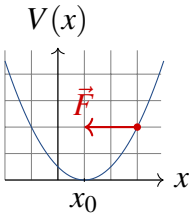
Potential energy surfaces
Analysis of potential energy surfaces leads to conclusions regarding the nature of bonding or dynamical behaviour of the molecular system. Let us introduce two important quantities: the *gradient vector* and the *force constant (or Hessian) matrix*.

$$\nabla U_a(R) = \{\partial U_a(R)/\partial R_1, \ldots, \partial U_a(R)/\partial R_{3N_{nuc}}\}$$
$$\kappa_{mn}^{(a)} = \frac{\partial U_a(R)}{\partial R_m \partial R_n} \quad (m,n = 1,\ldots,3N_{nuc})$$

3.104

3.6 Harmonic approximation

One-dimentional Harmonic oscillator



On a particle of mass m in the harmonic potential $V(x) = \frac{1}{2}k(x-x_0)^2$ distorted from the equilibrium $(x = x_0)$ acts a force proportional to the distortion

$$F = -\frac{dV}{dx} = -k(x-x_0)$$

Solutions to Schrödinger equation

$$\left(-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\chi_n(x) = \varepsilon_n\chi_n(x)$$

(for n=0,1,2,...) are

$$\chi_n(y) = A_n H_n(y) e^{-y^2/2}$$

where $y = \left(\frac{mk}{\hbar^2}\right)^{1/4} x$, $A_n = \sqrt{\frac{1}{\alpha\sqrt{\pi}2^n n!}}$ and $H_n(y) = (-1)^n e^{y^2}\frac{d^n}{dy^n}e^{-y^2}$ are the Hermite polynomials.

3.105

Properties of Hermite polynomials

$$H_n(y) = (-1)^n e^{y^2}\frac{d^n}{dy^n}e^{-y^2}$$

pseudo-orthogonality

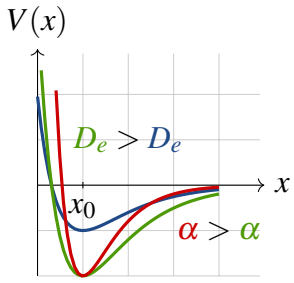
$$\int_{-\infty}^{\infty} H_m(y)H_n(y)e^{-y^2}\,dy = \sqrt{\pi}2^n n!\delta_{mn}$$

and recurrence

$$H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y)$$

3.106

Digression – The Morse Oscillator



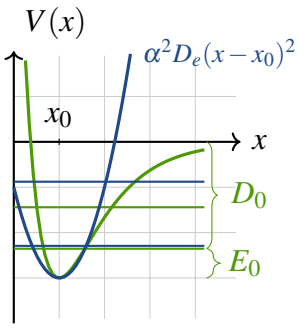
It turns out that the Schrödinger equation also has an analytical solution for the potential proposed by Morse, which provides a qualitatively correct description of bond dissociation in a molecule.

$$V(x) = D_e e^{-\alpha(x-x_0)} \left(e^{-\alpha(x-x_0)} - 2 \right)$$

Here, D_e is the depth of the potential well at its minimum, while the parameter α is related to the bond force constant and therefore to the width of the well.
By approximating the Morse potential with a harmonic potential having force constant k, we can determine the value of this constant from the second derivative of $V(x)$ at the minimum:

$$\left(\frac{d^2 V(x)}{dx^2} \right)_{x=x_0} = k = 2\alpha^2 D_e$$

3.107



Solutions exist for the ground state and for excited states; however, only a finite number of them are physically acceptable ($n = 0, 1, 2, \ldots, n_{max}$).

$$E_n = \hbar\omega_e \left(n + \frac{1}{2} \right) - \hbar\omega_e x_e \left(n + \frac{1}{2} \right)^2$$

In this expression, ω_e is the harmonic vibrational frequency, while x_e is the anharmonicity constant:

$$\omega = \sqrt{\frac{k}{\mu}} = \alpha \sqrt{\frac{2D_e}{\mu}}$$

$$x_e = \frac{\hbar\omega}{4D_e}$$

E_0 is the so-called *zero-point vibrational energy (ZPVE)*. Therefore, the dissociation energy is

$$D_0 = D_e - E_0$$

3.108

Harmonic approximation

In the vicinity of a stationary point $R^{(a)}$ one may expand the potential for nuclear motion into Taylor series with respect to small deviation of nuclear coordinates $\Delta R_n^{(a)} = R_n^{(a)} - R_n$ $(n = 1, \ldots, 3N_{nuc})$ from $R^{(a)}$. Since the gradient vector vanishes at $R^{(a)}$ the expantion truncated at a second order term is

$$U_a(R) = U_a(R^{(a)}) + \sum_{m,n=1}^{3N_{nuc}} \frac{1}{2} \kappa_{mn}^{(a)} \Delta R_m^{(a)} \Delta R_n^{(a)}$$

where the Hessian has to be taken at $R^{(a)}$. The Hamiltonian for the nuclear motion in the adiabatic approximation reads

$$H_a = U_a(R^{(a)}) + \sum_{n=1}^{3N_{nuc}} \frac{P_n^2}{2M_n} + \sum_{m,n=1}^{3N_{nuc}} \frac{1}{2} \kappa_{mn}^{(a)} \Delta R_m^{(a)} \Delta R_n^{(a)}$$

3.109

3.7 Normal mode analysis

It is convenient to diagonalize the kinetic and potential energy operators via the following linear transformation

$$\Delta R_n^{(a)} = \sum_{\xi} M_n^{-1/2} A_{n\xi}^{(a)} q_{a,\xi}$$

what leads to a following expression for H_a expressed in the so-called (mass-weighted) *normal mode coordinates*

$$H_a = U_a(q_{a,\xi} = 0) + H_a^{(mn)}$$

with the normal mode Hamiltonian

$$H_a^{(mn)} = \frac{1}{2} \sum_{\xi} \left(p_\xi^2 + \omega_{a,\xi}^2 q_{a,\xi}^2 \right)$$

In the above equation the harmonic normal-mode frequencies $\omega_{a,\xi}$ have been introduced.

3.110

$$H_a^{(mn)} = \frac{1}{2} \sum_{\xi} \left(p_\xi^2 + \omega_{a,\xi}^2 q_{a,\xi}^2 \right)$$

The nuclear motion can be understood as a superposition of independent harmonic vibrations around equilibrium geometry $R^{(a)}$ corresponding to $q_{a,\xi} = 0$. *The harmonic oscillations of individual atoms within a normal mode ξ have the same frequency $\omega_{a,\xi}$ but different amplitudes, determined by their masses.* In addition to $3N_{nuc} - 6$ normal mode freqencies will result in six eigenvalues equal to zero corresponding to free translations and rotations.

3.111

The nuclear Schrödinger equation can be solved for a given adiabatc electronic state by factorization with respect to the normal modes

$$H_a^{(mn)} \chi_{aN}^{(adia)}(q) = \varepsilon_{aN} \chi_{aN}^{(adia)}(q)$$

with

$$\chi_{aN}^{(adia)}(q) = \prod_{\xi} \chi_{aN_\xi}(q_{a,\xi})$$

where N is the set of quantum numbers $N = \{N_1, N_2, \ldots\}$ and the eigenfunctions for mode ξ are given by

$$\chi_{aN_\xi}(q_{a,\xi}) = \frac{\lambda_{a,\xi}}{\sqrt{\sqrt{\pi} 2^{N_\xi} N_\xi!}} \exp\left\{ \left(-\frac{1}{2} \lambda_{a,\xi}^2 q_{a,\xi}^2 \right) \right\} H_{N_\xi}(\lambda_{a,\xi} q_{a,\xi})$$

with $\lambda_{a,\xi}^2 = \omega_{a,\xi}/\hbar$ and H_{N_ξ} being the Hermite polynomials.

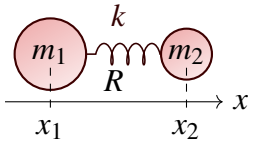
3.112

The eigenenergies read

$$\varepsilon_{aN} = \sum_{\xi} \hbar \omega_{a,\xi} \left(N_\xi + \frac{1}{2} \right)$$

3.113

Classical Description of Vibrations in a Diatomic Molecule



The classical displacement from the equilibrium position (R) is $q = x_2 - x_1 - R$. To express the Lagrangian, $L = T - V$, in terms of the generalized coordinate q and $\dot{q} = \frac{dq}{dt}$, we use:

$$\left.\begin{array}{l} \dot{q} = \dot{x}_2 - \dot{x}_1 \\ 0 = m_1 \dot{x}_1 + m_2 \dot{x}_2 \end{array}\right\} \rightsquigarrow \left\{\begin{array}{l} \dot{x}_1 = \frac{-m_2}{m_1+m_2} \dot{q} \\ \dot{x}_2 = \frac{m_1}{m_1+m_2} \dot{q} \end{array}\right.$$

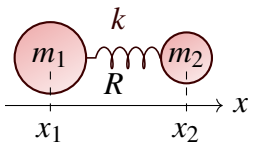
Introducing the reduced mass $\mu = \frac{m_1 m_2}{m_1+m_2}$, we obtain:

$$\left.\begin{array}{l} T = \frac{1}{2} m_1 \dot{x}_1^2 + \frac{1}{2} m_2 \dot{x}_2^2 \\ V = \frac{1}{2} k q^2 \end{array}\right\} \rightsquigarrow \left\{\begin{array}{l} T = \frac{1}{2} \mu \dot{q}^2 \\ V = \frac{1}{2} k q^2 \end{array}\right.$$

It remains to solve the Lagrange equations of motion:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0, \qquad i = 1, 2, \ldots, f$$

3.114



In our case, the number of degrees of freedom is $f = 1$ and $q_1 = q$, therefore:

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}}\right) - \frac{\partial T}{\partial q} = -\frac{\partial V}{\partial q}$$

Finally, we obtain exactly the same equation of motion as for an oscillating block of mass μ:

$$\mu\ddot{q} - 0 = -kq$$

3.115

Example: Vibrational Modes of the Water Molecule (H_2O)
The H_2O molecule is nonlinear (bond angle approximately 104.5°). It is convenient to use internal coordinates (bond lengths + bond angle).

Three Main Vibrational Modes

1. v_1 – symmetric O–H stretching,
2. v_2 – bending vibration (change of the H–O–H angle),
3. v_3 – asymmetric O–H stretching.

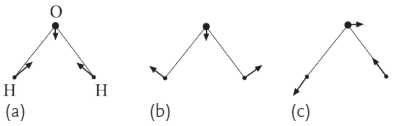


Figure 1: Displacement vectors corresponding to the three normal coordinates of the water molecule (a)–(c). Differences in amplitudes arise from differences in atomic masses.

3.116

Internal Coordinates
We consider a molecule confined to a plane:

- r_1 – length of the first O–H bond,
- r_2 – length of the second O–H bond,
- α – H–O–H bond angle.

Vibrations relative to the equilibrium geometry are described by internal coordinates q_i:

$$q_1 = \Delta r_1, \quad q_2 = \Delta r_2, \quad q_3 = \Delta\alpha.$$

Collecting them into a vector:

$$\mathbf{q} = \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta\alpha \end{pmatrix}.$$

3.117

Potential Energy
Within the small-amplitude approximation:

$$V(\mathbf{q}) \approx \frac{1}{2}\sum_{i,j=1}^{3} k_{ij} q_i q_j = \frac{1}{2}\mathbf{q}^{\mathrm{T}}\mathbf{K}\,\mathbf{q}.$$

For a simple H_2O model:

$$V = \frac{1}{2}\left(k_r q_1^2 + k_r q_2^2 + 2k_{rr} q_1 q_2 + k_\alpha q_3^2\right),$$

$$\mathbf{K} = \begin{pmatrix} k_r & k_{rr} & 0 \\ k_{rr} & k_r & 0 \\ 0 & 0 & k_\alpha \end{pmatrix}.$$

- k_r – force constant of a single O–H bond,
- k_{rr} – coupling between the two bonds,
- k_α – stiffness of the H–O–H bond angle.

3.118

Kinetic Energy

The kinetic energy in internal coordinates is a quadratic form:

$$T = \frac{1}{2}\dot{\mathbf{q}}^{\mathrm{T}}\mathbf{A}\,\dot{\mathbf{q}}.$$

In a simple planar model:

$$T = \frac{1}{2}\left[\mu(\dot{q}_1^2 + \dot{q}_2^2) + \mu_\alpha \dot{q}_3^2\right],$$

$$\mathbf{A} = \begin{pmatrix} \mu & 0 & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \mu_\alpha \end{pmatrix}.$$

- μ – effective (reduced) mass for O–H stretching,
- μ_α – effective mass for bending motion.

3.119

Lagrangian and Equations of Motion

$$L = T - V = \frac{1}{2}\dot{\mathbf{q}}^{\mathrm{T}}\mathbf{A}\,\dot{\mathbf{q}} - \frac{1}{2}\mathbf{q}^{\mathrm{T}}\mathbf{K}\,\mathbf{q}.$$

The starting point is the Euler–Lagrange equations for small vibrations. Recall that the Lagrangian is a scalar. Consider the potential-energy contribution:

$$V = \frac{1}{2}\mathbf{q}^T\mathbf{K}\mathbf{q},$$

The gradient is evaluated component-wise with respect to

$$\mathbf{q} = (q_1, \ldots, q_n)^T :$$

$$\frac{\partial V}{\partial q_k} = \frac{1}{2}\sum_{i,j} K_{ij}\frac{\partial (q_i q_j)}{\partial q_k} = \sum_j K_{kj} q_j.$$

This is simply the kth component of the vector $\mathbf{Kq}$.

Similarly, differentiating T with respect to the generalized momenta yields:

$$\frac{d}{dt}(\mathbf{A}\,\dot{\mathbf{q}}) + \mathbf{K}\,\mathbf{q} = 0.$$

3.120

Lagrangian and Equations of Motion
Assume harmonic solutions:

$$\mathbf{q}(t) = \mathbf{a}\cos(\omega t) \quad \Rightarrow \quad \ddot{\mathbf{q}} = -\omega^2 \mathbf{q}.$$

Substitution gives:

$$-\omega^2 \mathbf{A}\,\mathbf{a} + \mathbf{K}\,\mathbf{a} = 0.$$

$$\left(\mathbf{K} - \omega^2 \mathbf{A}\right)\mathbf{a} = 0.$$

Nontrivial solutions exist only if

$$\boxed{\det\left(\mathbf{K} - \omega^2 \mathbf{A}\right) = 0}$$

This is a generalized **eigenvalue problem**, where:

- the eigenvalues ω^2 give the normal-mode frequencies,
- the eigenvectors $\mathbf{a}$ define the vibrational patterns.

3.121

Bending Mode
From the structure of the matrices:

$$\mathbf{K} = \begin{pmatrix} \boxed{\begin{matrix} k_r & k_{rr} \\ k_{rr} & k_r \end{matrix}} & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & 0 \end{matrix} & k_\alpha \end{pmatrix},$$

$$\mathbf{A} = \begin{pmatrix} \boxed{\begin{matrix} \mu & 0 \\ 0 & \mu \end{matrix}} & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & 0 \end{matrix} & \mu_\alpha \end{pmatrix}$$

it is clear that q_3 (the angle coordinate) does not mix with q_1 and q_2:

$$(k_\alpha - \omega^2 \mu_\alpha) a_3 = 0 \Rightarrow \omega_2^2 = \frac{k_\alpha}{\mu_\alpha}.$$

$$\mathbf{a}^{(2)} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad \Rightarrow \quad Q_2 \sim \Delta\alpha.$$

This corresponds to the **bending mode** (H–O–H angle vibration). 3.122

Two Stretching Modes
For the stretching subspace (the first two coordinates), we solve

$$\det \begin{pmatrix} k_r - \omega^2 \mu & k_{rr} \\ k_{rr} & k_r - \omega^2 \mu \end{pmatrix} = 0,$$

which gives

$$(k_r - \omega^2\mu)^2 - k_{rr}^2 = 0 \Rightarrow k_r - \omega^2\mu = \pm k_{rr}.$$

Thus, two vibrational frequencies are obtained:

$$\omega_1^2 = \frac{k_r + k_{rr}}{\mu}, \qquad \omega_3^2 = \frac{k_r - k_{rr}}{\mu}.$$

3.123

Eigenvectors – Vibrational Patterns

Symmetric Stretching (ω_1)
For $\omega_1^2 = \frac{k_r+k_{rr}}{\mu}$ we obtain

$$a_1 = a_2 \quad \Rightarrow \quad \mathbf{a}^{(1)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}.$$

Both O–H bonds lengthen and shorten **in phase**.

Asymmetric Stretching (ω_3)
For $\omega_3^2 = \frac{k_r-k_{rr}}{\mu}$ we obtain

$$a_1 = -a_2 \quad \Rightarrow \quad \mathbf{a}^{(3)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}.$$

One O–H bond lengthens while the other shortens – **out-of-phase motion**.

3.124

Normal Coordinates
The transformation matrix (columns = eigenvectors) is

$$\mathbf{S} = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \end{pmatrix}.$$

We define the normal coordinates as

$$\mathbf{Q} = \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \mathbf{S}^{\mathrm{T}}\mathbf{q}.$$

This yields

$$Q_1 = \frac{1}{\sqrt{2}}(q_1 + q_2) \quad \text{(symmetric stretching)},$$

$$Q_3 = \frac{1}{\sqrt{2}}(q_1 - q_2) \quad \text{(asymmetric stretching)},$$

$$Q_2 = q_3 = \Delta\alpha \quad \text{(bending)}.$$

3.125

Hamiltonian in Normal Coordinates

After appropriate scaling to mass-weighted coordinates, the kinetic energy becomes

$$T = \frac{1}{2}\sum_{k=1}^{3} \dot{Q}_k^2,$$

while the potential energy is

$$V = \frac{1}{2}\sum_{k=1}^{3} \omega_k^2 Q_k^2.$$

We define the canonical momenta

$$P_k = \frac{\partial L}{\partial \dot{Q}_k} = \dot{Q}_k.$$

The Hamiltonian takes the form

$$H = \sum_{k=1}^{3} \left(\frac{1}{2}P_k^2 + \frac{1}{2}\omega_k^2 Q_k^2 \right). \qquad 3.126$$

Physical Interpretation

- The H_2O molecule possesses three independent normal vibrations:

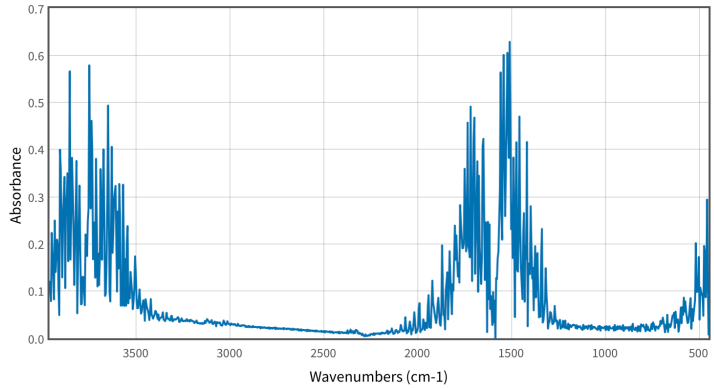
$$Q_1 \leftrightarrow v_1 \text{ (symmetric stretching)}$$
$$Q_2 \leftrightarrow v_2 \text{ (bending)}$$
$$Q_3 \leftrightarrow v_3 \text{ (asymmetric stretching)}.$$

- In normal coordinates, the Hamiltonian is a sum of three independent harmonic oscillators.
- Therefore, in the quantum-mechanical description,

$$E_{v_1 v_2 v_3} = \hbar\omega_1 \left(v_1 + \tfrac{1}{2}\right) + \hbar\omega_2 \left(v_2 + \tfrac{1}{2}\right) + \hbar\omega_3 \left(v_3 + \tfrac{1}{2}\right). \qquad 3.127$$

- A nonlinear triatomic molecule (such as H_2O) possesses three independent normal vibrations.
- By using internal coordinates and the matrices $\mathbf{A}$ and $\mathbf{K}$, the problem is reduced to a generalized eigenvalue problem.
- The normal coordinates Q_k diagonalize both the kinetic and potential energies.
- The Hamiltonian becomes a sum of independent harmonic oscillators. 3.128

IR Spectrum of the H_2O Molecule



The IR spectrum of water consists of two contributions:

- **Intramolecular vibrations:**

$$\begin{aligned} \nu_1 &\approx 3657\ \mathrm{cm}^{-1} \quad \text{(symmetric stretching)} \\ \nu_2 &\approx 1595\ \mathrm{cm}^{-1} \quad \text{(H–O–H bending)} \\ \nu_3 &\approx 3756\ \mathrm{cm}^{-1} \quad \text{(asymmetric stretching)} \end{aligned}$$

- **Collective vibrations** associated with the hydrogen-bond network (present only in the liquid phase).

3.129

Franck-Condon approximation

Let us establish the relation between normal modes belonging to different electronic states.

Since we have performed a normal mode analysis for the electronic ground state PES, $U_{a=g}(R)$, which has a minimum at $R^{(g)}$ we can perform similar analysis for the excited state PES $U_{a=e}(R)$ accessible from the ground state via an optical transition in the vicinity of $R^{(e)}$.

$$U_e(R) = U_e(R^{(e)}) + \sum_{m,n=1}^{3N_{nuc}} \frac{1}{2} \kappa_{mn}^{(e)} \Delta R_m^{(e)} \Delta R_n^{(e)}$$

3.130

We can relate the displacement vectors for the excited state to those for the ground state, assuming that the same linear transformation of the Cartesian displacements, $A_{n\xi}^{(g)}$ diagonalizes Hamiltonian for both states simultaneously

$$\Delta R_n^{(e)} = R_n - R_n^{(g)} - (R_n^{(e)} - R_n^{(g)}) = \sum_{\xi} M_n^{-1/2} A_{n\xi}^{(g)} (q_{g,\xi} - q_{e,\xi})$$

3.131

Allowing for state-dependent normal mode frequencies, $\omega_{a,\xi}$ we can write the Hamiltonian for the excited state as

$$H_e = U_e(q_\xi = q_\xi^{(e)}) + \frac{1}{2}\sum_\xi \left(p_\xi^2 + \omega_{e,\xi}^2 (q_\xi - q_\xi^{(e)})^2 \right)$$

where $q_{g,\xi} = q_{e,\xi} = q_\xi$ and $q_\xi^{(e)} = \Delta q_{e,\xi}$.

The solutions of the stationary Schrödinger equation for the excited state are now shifted oscillator states.

$$\chi_{eN_\xi}(q_\xi) = \frac{\lambda_{e,\xi}}{\sqrt{\sqrt{\pi} 2^{N_\xi} N_\xi!}} \exp\left\{ \left(-\frac{1}{2}\lambda_{e,\xi}^2 (q_\xi - q_\xi^{(e)})^2 \right) \right\} \times H_{N_\xi}(\lambda_{e,\xi}(q_\xi - q_\xi^{(e)})) \qquad 3.132$$

Assuming $|\chi_{aM}\rangle$ and $|\chi_{bN}\rangle$ to be two normal mode eigenstates for a particular mode belonging to the electronic states a and b, one may derive an expression for the overlap integral called the *Franck-Condon factor*

$$\langle \chi_{aM} | \chi_{aN} \rangle = \exp\left\{ \left(\frac{-(\Delta g_{ab})^2}{2} \right) \right\} \sum_{m=0}^{M} \sum_{n=0}^{N} \frac{(-1)^n (\Delta g_{ab})^{m+n}}{m! n!} \times \sqrt{\frac{M! N!}{(M-m)!(N-n!)}} \delta_{M-m,N-n}$$

where $\Delta g_{ab} = g_a - g_b$ and $g_a(\xi) = -\sqrt{\frac{\omega_\xi}{2\hbar}} q_\xi^{(a)}$ is the dimensionless shift of the potential energy surface belonging to state a.

Due to the exponential prefactor for any given pair of states, the overlap (and hence the coupling) decreases upon increasing the shift between the two PESs. 3.133

3.8 Hamiltonian in diabatic representation

Diabatic representation of the molecular Hamiltonian
The general form of the molecular wave function is given as a following projection to a complete set of adiabatic electronic states:

$$\psi_{mol}(r;R) = \sum_a \chi_{aM}(R)\phi_a(r;R)$$

The representation of the molecular Hamiltonian in this electronic basis is then obtained as

$$H_{mol} = \sum_{a,b}(\delta_{ab}H_a(R) + (1-\delta_{ab})\Theta_{ab}|\phi_a\rangle\langle\phi_b|$$

where $H_a(R)$ and Θ_{ab} are still operators with respect to the nuclear coordinates.

3.134

If we expand the Hamiltonian in the basis of adiabatic states $|\psi_{aM}\rangle = |\phi_a\rangle|\chi_{aM}\rangle$ which define the Born–Oppenheimer wave function

$$H_{mol} = \sum_{a,M} \varepsilon_{aM}|\psi_{aM}\rangle\langle\psi_{aN}| + \sum_{aM,bN} \Theta_{aM,bN}|\psi_{aM}\rangle\langle\psi_{bN}|$$

where

$$\Theta_{aM,bN} = \int dR\, \chi^*_{aM}(R)\left[\langle\phi_a|T_n|\phi_b\rangle - \sum_n \frac{1}{M_n}\langle\phi_a|\nabla_n|\phi_b\rangle\nabla_n\right]\chi_{bN}(R)$$

The coupling is mediated by the momentum operator (*dynamic coupling*) and its calculation requires knowledge of the 1st and 2nd derivatives of the electronic wave function.

3.135

The dynamic coupling is often sharply peaked if not singular, indicating that the character of the electronic wave function changes rapidly within a narrow range of configuration space.

3.136

An alternative to the adiabatic representation of the Hamiltonian is the so-called *diabatic representation* or *crude adiabatic representation*.

Let us consider an electronic basis $\phi_a(r;R^{(0)})$, where the positions of the nuclei are fixed at some point $R^{(0)}$ in the configuration space. $\phi_a(r;R^{(0)})$ is no longer an eigenfunction of $H_{el}(R)$ except at $R^{(0)}$. Defining $H_{el}(R^{(0)}) = H^{(0)}$ the electronic Hamiltonian can be written as

$$H_{el}(R) = H^{(0)}(R^{(0)}) + V(R,R^{(0)})$$

with the *potential coupling*

$$V(R,R^{(0)}) = H_{el}(R) - H^{(0)}(R^{(0)})$$

The molecular wave function in this *diabatic* basis set becomes

$$\psi(r;R) = \sum_{\bar{a}} \chi_{\bar{a}}(R)\phi_{\bar{a}}(r;R^{(0)})$$

3.137

In diabatic representation all matrix elements of the nonadiabaticity operator vanish because the diabatic basis functions are not R-dependent. The coupling between different electronic states is now due to $V(R,R^{(0)})$ operator whose matrix elements are $V_{\bar{a}\bar{b}}(R,R^{(0)}) = \langle\phi_{\bar{a}}|V(R,R^{(0)})|\phi_{\bar{b}}\rangle$. Thus the representation of the molecular Hamiltonian in terms of the diabatic electronic states is

$$H_{mol} = \sum_{\bar{a},\bar{b}} (\delta_{\bar{a}\bar{b}}H_{\bar{a}} + (1-\delta_{\bar{a}\bar{b}})V_{\bar{a}\bar{b}})\,|\phi_{\bar{a}}\rangle\langle\phi_{\bar{b}}|$$

where

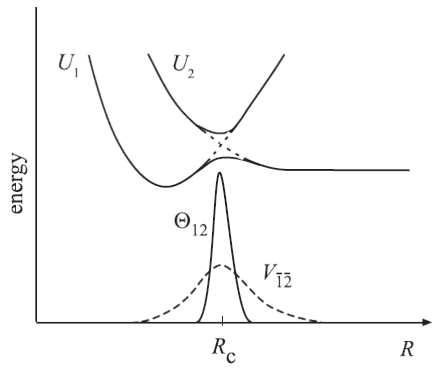
$$H_{\bar{a}}(R) = T_n + U_{\bar{a}}(R)$$

is the Hamiltonian for nuclear motion in diabatic state $\langle\phi_{\bar{a}}|$ with the diabatic PES

$$U_{\bar{a}}(R) = E_{\bar{a}}(R^{(0)}) + V_{nn} + V_{\bar{a}\bar{a}}(R,R^{(0)})$$

3.138

Noncrossing rule



The diabatic potential energy curves (dashed line) intersect at R_c. The crossing condition $U_{\bar{a}}(R) = U_{\bar{b}}(R)$ can in principle be fulfilled for any R. However, if one incorporates the diabatic state coupling $V_{\bar{a}\bar{b}}$ the potential curves of the diagonalized diabatic Hamiltonian show an *avoided crossing*. This behavior (solid lines) is due to the fact that the conditions $U_{\bar{a}}(R) = U_{\bar{b}}(R)$ and $V_{\bar{a}\bar{b}}(R) = 0$ cannot be fulfilled simultaneously unless $V_{\bar{a}\bar{b}}(R)$ vanishes due to the symmetry of diabatic wavefunctions.
Since diabatic and adiabatic Hamiltonians describe the same molecular system, the *adiabatic potential curves of states having the same symmetry will not cross as well*.

3.139

Conical intersections
The situation is different in polyatomic molecules. Here the crossing conditions $U_{\bar{b}}(R)$ and $V_{\bar{a}\bar{b}}(R) = 0$ can be simultaneously fulfilled even for states having the same symmetry. *For an N-dimensional PES the crossing will only be in $N-2$ (or if $V_{\bar{a}\bar{b}}(R) = 0$ due to symmetry the crossing is in $N-1$ dimensions only)*.

For instance, in the two-dimensional case the PESs of two electronic states of the same symmetry will intersect at a single point ($N-2=0$). The topology of the PES in the vicinity of this point is usually called a *conical intersection* (first discussed by E. Teller in 1937).

3.140

Mixing angle
Within the coupled two-states problem (which is exactly solvable) the diabatic states can be expanded in terms of the adiabatic states:

$$\phi_{\bar{a}}(r;R) = \sum_{a=1,2} C_{\bar{a}}(a)\phi_a(r;R)$$

the coefficients $C_{\bar{a}}$ depend on the so-called mixing angle $\bar{\gamma}(R)$ which is chosen to eliminate the dynamic coupling

$$\sum_n \langle \phi_{\bar{a}} | \nabla_n | \phi_{\bar{b}} \rangle = 0$$

Inserting expansion of $\phi_{\bar{a}}(r;R)$ to the above equation yields

$$-\sum_n \nabla_n \bar{\gamma}(R) = -\sum_n \langle \phi_{\bar{a}} | \nabla_n | \phi_{\bar{b}} \rangle$$

which has a unique solution only for a single nuclear degree of freedom.

3.141

An alternative can be developed by starting from a diabatic basis that is constructed in such a way that certain properties such as the dipole moments of the molecule behave smoothly. A related constraint is that the electronic wave function should not change appreciably when moving in the configuration space of the nuclear coordinates.

Given the diabatic Hamiltonian, the related mixing angle $\gamma(R)$ of the diabatic to adiabatic back transformation (diagonalizing potential energy operator) is given by

$$\gamma(R) = \frac{1}{2}\arctan\frac{2|V_{\bar{1}\bar{2}}(R)|}{|U_{\bar{1}}(R) - U_{\bar{2}}(R)|}$$

and the adiabatic potential then reads

$$U_{1/2}(R)\frac{1}{2}\left(U_{\bar{1}}(R) + U_{\bar{2}}(R) \pm \sqrt{(U_{\bar{1}}(R) - U_{\bar{2}}(R))^2 + 4|V_{\bar{1}\bar{2}}(R)|^2}\right)$$

3.142

Adiabatic vs. diabatic representation

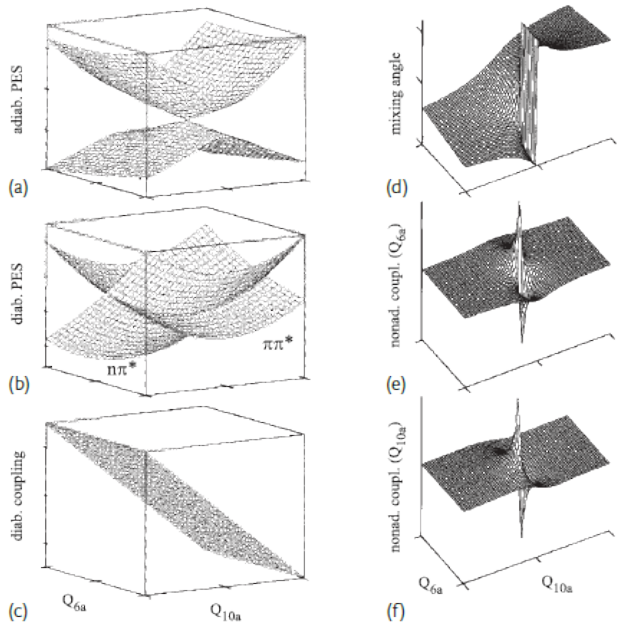
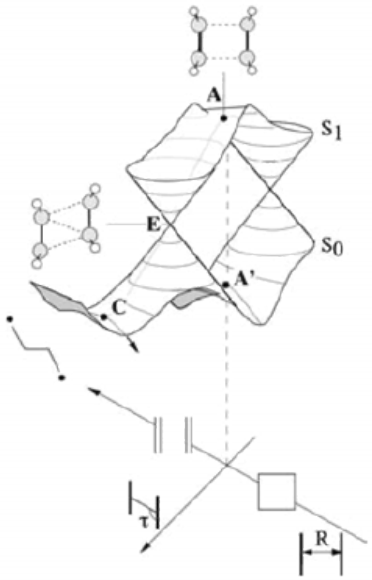


Figure 2: Results of quantum chemical calculations of the potential energy surfaces for the S_1 ($n\pi^*$) and S_2 ($\pi\pi^*$) electronic states of pyrazine along the Q_{6a} and Q_{10a} normal mode coordinates of the electronic ground state. (a) Adiabatic PES showing a conical intersection, (b) diabatic PES, (c) coupling between diabatic electronic states ($V_{\bar{1}\bar{2}}$), (d) mixing angle, (e) and (f) singular part of the nonadiabatic coupling given as the derivative of the mixing angle with respect to the two normal mode coordinates.

3.143

The photochemical cycloaddition of two ethylenes



The obvious choice of reaction coordinate is **R**, the interfragment separation. This coordinate brings the two ethylenes together face-to-face in a Woodward-Hoffman allowed process. Woodward-Hoffman theory predicts that along this coordinate there will be a minimum **A** on the excited state, and a corresponding maximum **A'** on the ground state. The 2nd coordinate is a rhomboidal distortion τ, orthogonal to **R**. Now **A** (which was a minimum along **R** alone) becomes a transition structure, and the negative direction of curvature leads through a surface crossing **E** (a conical intersection) into the region of an open tetramethylene biradicaloid **C** on the ground state. Thus, ground-state photochemical products are produced by decay of the excited state through a conical intersection.

3.144

Chapter 4
Electronic structure calculation methods

4.145

4.1 Variational Method

In the variational method, we use the fact that the functional

$$\varepsilon[\phi_t] = \frac{\langle \phi_t | H \phi_t \rangle}{\langle \phi_t | \phi_t \rangle} \geq E_0$$

is bounded from below by the ground-state energy E_0. Therefore, if we start from the so-called trial function $\phi_t(x_1, \ldots, x_n; c_1, \ldots, c_m)$, where $\{x_i\}$ are generalized coordinates (e.g., for electrons) and $\{c_i\}$ is the set of so-called variational parameters, then solving the eigenvalue problem reduces to minimizing the functional $\varepsilon[\phi_t]$.

4.146

Naturally, the trial function must be a "proper" function but is otherwise essentially arbitrary. The closer it is to the actual ground-state wavefunction, the better the result. If we now substitute our function into the functional $\varepsilon[\phi]$ and compute the integrals, we obtain the function $\varepsilon(c_1, \ldots, c_m)$, which depends on the variational parameters. What remains is to find its optimal form, i.e., the set of parameters $\{c_i\}$ that minimizes the value of $\varepsilon[\phi]$. In this way, we determine an approximate form of the wavefunction and the ground-state energy:

$$\frac{\partial \varepsilon(c_1, \ldots, c_m)}{\partial c_1} = \frac{\partial \varepsilon(c_1, \ldots, c_m)}{\partial c_2} = \ldots = \frac{\partial \varepsilon(c_1, \ldots, c_m)}{\partial c_m} = 0.$$

4.147

Example 1
Let us assume that we do not know the exact solutions for the hydrogen atom and seek them by assuming an exponential wave-function:

$$\psi(r) = Ne^{-ar}.$$

Determine the value of the variational parameter a. We write the Hamiltonian in spherical coordinates as:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{e^2}{r}.$$

However, since our function does not depend on the angles θ and ϕ, we can write the Hamiltonian in the simpler form:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)\right] - \frac{e^2}{r}.$$

4.148

The energy functional can be written as:

$$\begin{aligned}
\varepsilon[\psi] &= \frac{\langle\psi|\hat{H}\psi\rangle}{\langle\psi|\psi\rangle} \\
&= \frac{N^2\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-ar}\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)\right] - \frac{e^2}{r}\right\}e^{-ar}r^2\sin\theta\,dr\,d\theta\,d\phi}{N^2\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-2ar}r^2\sin\theta\,dr\,d\theta\,d\phi} \\
&= \frac{\hbar^2}{2\mu}a^2 - ae^2.
\end{aligned}$$

It remains to find the optimal value of the parameter a and the corresponding eigenvalue:

$$\frac{d\varepsilon}{da} = 0 = \frac{\hbar^2}{\mu}a - e^2 \quad \rightsquigarrow \quad a = \frac{e^2\mu}{\hbar^2} \quad \rightsquigarrow \quad E_1 = -\frac{e^4\mu}{2\hbar^2}.$$

Thus, we obtain the identical solution to the analytical one.

4.149

4.2 Molecular Orbital Method

Ritz Method – A Special Case of the Variational Method
In this method, the trial function Ψ is assumed to be a linear combination of known functions ϕ (e.g., atomic orbitals):

$$\Psi = c_1\phi_1 + c_2\phi_2 + \ldots + c_n\phi_n = \sum_{i=1}^{n} c_i\phi_i, \tag{1}$$

where $\{c_i\}$ is the set of variational parameters. If H is the Hamiltonian of the system, then the energy functional can be written as:

$$\varepsilon(\Psi) = \frac{\left\langle \sum_{i=1}^{n} c_i\phi_i \middle| H \middle| \sum_{i=1}^{n} c_i\phi_i \right\rangle}{\left\langle \sum_{i=1}^{n} c_i\phi_i \middle| \sum_{i=1}^{n} c_i\phi_i \right\rangle} = \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j H_{ij}}{\sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j S_{ij}},$$

where $H_{ij} = \langle\phi_i|H|\phi_j\rangle$ and $S_{ij} = \langle\phi_i|\phi_j\rangle$. 4.150
This result can be written more compactly as follows:

$$\varepsilon \sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j S_{ij} = \sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j H_{ij}. \tag{2}$$

We seek the minimum of the energy functional with respect to all variational parameters. Hence:

$$\frac{\partial\varepsilon}{\partial c_i} = 0 \quad \text{for} \quad i = 1,2,\ldots,n. \tag{3}$$

To find the variational parameters, let us differentiate Eq. (2) with respect to all variational parameters (e.g., c_i^*):

$$\frac{\partial}{\partial c_i^*}\Big(\varepsilon \sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j S_{ij}\Big) = \frac{\partial}{\partial c_i^*}\Big(\sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j H_{ij}\Big).$$

4.151

$$\frac{\partial\varepsilon}{\partial c_i^*}\sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j S_{ij} + \varepsilon\frac{\partial}{\partial c_i^*}\sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j S_{ij} = \frac{\partial}{\partial c_i^*}\sum_{i=1}^{n}\sum_{j=1}^{n} c_i^* c_j H_{ij}.$$

Using (3), we get a system of linear equations:

$$\varepsilon\sum_{j=1}^{n} c_j S_{ij} = \sum_{j=1}^{n} c_j H_{ij} \quad \text{for} \quad i = 1,2,\ldots,n,$$

which can also be written as:

$$\sum_{j=1}^{n} c_j\big(H_{ij} - \varepsilon S_{ij}\big) = 0 \quad \text{for} \quad i = 1,2,\ldots,n. \tag{4}$$

4.152

Minimizing the energy functional with the trial function of the form (1) thus reduces to solving a homogeneous system of n linear equations in which the unknowns are the coefficients of the linear combination $\{c_i\}$:

$$\begin{aligned}
&c_1\big(H_{11} - \varepsilon S_{11}\big) + c_2\big(H_{12} - \varepsilon S_{12}\big) + \ldots + c_n\big(H_{1n} - \varepsilon S_{1n}\big) = 0\\
&c_1\big(H_{21} - \varepsilon S_{21}\big) + c_2\big(H_{22} - \varepsilon S_{22}\big) + \ldots + c_n\big(H_{2n} - \varepsilon S_{2n}\big) = 0\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
&c_1\big(H_{n1} - \varepsilon S_{n1}\big) + c_2\big(H_{n2} - \varepsilon S_{n2}\big) + \ldots + c_n\big(H_{nn} - \varepsilon S_{nn}\big) = 0
\end{aligned}$$

Since the above equations lack constant terms (this is a homogeneous system), they provide only the relative values of the variational parameters: $\frac{c_2}{c_1}, \frac{c_3}{c_1}$, etc.

4.153

The wavefunction normalization condition supplies the missing non-homogeneous equation:

$$\langle \Psi | \Psi \rangle = \left\langle \sum_{i=1}^{n} c_i \phi_i \middle| \sum_{j=1}^{n} c_j \phi_j \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} c_i^* c_j S_{ij} = 1.$$

Non-trivial solutions of the system of equations (5) exist if the determinant formed from the coefficients of the unknowns vanishes:

$$\begin{vmatrix} H_{11} - \varepsilon S_{11} & H_{12} - \varepsilon S_{12} & \dots & H_{1n} - \varepsilon S_{1n} \\ H_{21} - \varepsilon S_{21} & H_{22} - \varepsilon S_{22} & \dots & H_{2n} - \varepsilon S_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} - \varepsilon S_{n1} & H_{n2} - \varepsilon S_{n2} & \dots & H_{nn} - \varepsilon S_{nn} \end{vmatrix} = 0.$$

4.154

Ultimately, solving the system of equations $\sum_{j=1}^{n} c_j \left(H_{ij} - \varepsilon S_{ij} \right) = 0$ for $i = 1, 2, \dots, n$ reduces to expanding the determinant

$$\begin{vmatrix} H_{11} - \varepsilon S_{11} & H_{12} - \varepsilon S_{12} & \dots & H_{1n} - \varepsilon S_{1n} \\ H_{21} - \varepsilon S_{21} & H_{22} - \varepsilon S_{22} & \dots & H_{2n} - \varepsilon S_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} - \varepsilon S_{n1} & H_{n2} - \varepsilon S_{n2} & \dots & H_{nn} - \varepsilon S_{nn} \end{vmatrix} = 0$$

and finding the values of the parameters $\{c_i\}$ using the equation:

$$\sum_{i=1}^{n} \sum_{j=1}^{n} c_i^* c_j S_{ij} = 1.$$

4.155

The Ritz method simplifies greatly if the functions $\{\phi_i\}$ form an orthonormal set, i.e.,

$$\langle \phi_i | \phi_j \rangle = S_{ij} = \delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j, \\ 0 & \text{if} \quad i \neq j, \end{cases}$$

leading to the following system of equations:

$$\sum_{j=1}^{n} c_j \left(H_{ij} - \varepsilon \delta_{ij} \right) = 0 \quad \text{for} \quad i = 1, 2, \dots, n.$$

4.156

A Simple Case

Let us find the energy values for a trial function of the form (e.g., for the hydrogen molecule in a minimal basis of 1s orbitals):

$$\Psi = c_1\phi_1 + c_2\phi_2.$$

We may assume that

$$\begin{aligned} H_{11} &= H_{22}, & H_{12} &= H_{21}, \\ S_{11} &= S_{22} = 1, & S_{12} &= S_{21} = S. \end{aligned}$$

The secular system can be written as:

$$\begin{aligned} c_1\big(H_{11}-\varepsilon\big) &+ c_2\big(H_{12}-\varepsilon S\big) &&= 0 \\ c_1\big(H_{12}-\varepsilon S\big) &+ c_2\big(H_{11}-\varepsilon\big) &&= 0 \end{aligned} \qquad 4.157$$

The secular determinant is:

$$\begin{vmatrix} H_{11}-\varepsilon & H_{12}-\varepsilon S \\ H_{12}-\varepsilon S & H_{11}-\varepsilon \end{vmatrix} = 0 \rightsquigarrow \big(H_{11}-\varepsilon\big)^2 = \big(H_{12}-\varepsilon S\big)^2.$$

Hence we get two possible values of ε (E_1 and E_2):

$$E_1 = \frac{H_{11}+H_{12}}{1+S}, \quad E_2 = \frac{H_{11}-H_{12}}{1-S}.$$

Substituting E_1 back into the system of equations gives $c_{11} = c_{21}$, whereas for E_2 it yields $c_{12} = -c_{22}$. From the normalization condition $c_1^2 + 2c_1c_2S + c_2^2 = 1$, we get specific values:

$$\begin{aligned} c_{11} = c_{21} &= \frac{1}{\sqrt{2(1+S)}}, \\ c_{12} = -c_{22} &= \frac{1}{\sqrt{2(1-S)}}. \end{aligned} \qquad 4.158$$

4.3 Perturbation Theory

Rayleigh–Schrödinger Perturbation Theory
We can use perturbation theory when we want to solve the Schrödinger equation for the k-th state

$$\hat{H}\psi_k = E\psi_k$$

and at the same time can find a solution for a slightly simplified problem

$$\hat{H}^{(0)}\psi_k^{(0)} = E_k^{(0)}\psi_k^{(0)}$$

and express the Hamiltonian $\hat{H}$ of our problem in the following form:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)},$$

where $\hat{H}^{(0)}$ is the Hamiltonian for which we can solve the Schrödinger equation (called the unperturbed operator), and $\hat{H}^{(1)}$ represents a small perturbation to our system.

4.159

We assume that the functions $\psi_k^{(0)}$ form an orthonormal set, and for simplification of calculations we can also adopt the so-called intermediate normalization:

$$\langle\psi_k^{(0)}|\psi_k\rangle = 1,$$

which allows us to express the desired wave function as an expansion:

$$\psi_k = \psi_k^{(0)} + \textit{orthogonal terms}.$$

We now introduce an arbitrary parameter $0 \leq \lambda \leq 1$ in the Hamiltonian:

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda\hat{H}^{(1)} + \lambda^2\hat{H}^{(2)},$$

leading to:

$$\hat{H}(\lambda)\,\psi_k(\lambda) = E(\lambda)\,\psi_k(\lambda)$$

4.160

Introducing the parameter λ allows us to expand the energy and the wave function in a Taylor series — this is the so-called perturbative expansion:

$$E_k(\lambda) = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \ldots$$
$$\psi_k(\lambda) = \psi_k^{(0)} + \lambda\psi_k^{(1)} + \lambda^2\psi_k^{(2)} + \ldots$$

Substituting into the Schrödinger equation reveals that the equation is satisfied only if the coefficients of like powers of λ on both sides are equal:

$$\left(\hat{H}^{(0)} + \lambda\hat{H}^{(1)}\right)\left(\psi_k^{(0)} + \lambda\psi_k^{(1)} + \lambda^2\psi_k^{(2)} + \ldots\right) =$$
$$\left(E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \ldots\right)\left(\psi_k^{(0)} + \lambda\psi_k^{(1)} + \lambda^2\psi_k^{(2)} + \ldots\right)$$

4.161

Formally, this leads to infinitely many equations, but in practice we can solve them successively, finding successive corrections to the energy and wave function (typically, very good results are obtained already at second order for energy and first order for the wave function):

$$\begin{aligned}
&\lambda^0 \left(\hat{H}^{(0)} \psi_k^{(0)} - E_k^{(0)} \psi_k^{(0)} \right) + \\
&\lambda^1 \left(\hat{H}^{(0)} \psi_k^{(1)} + \hat{H}^{(1)} \psi_k^{(0)} - E_k^{(0)} \psi_k^{(1)} - E_k^{(1)} \psi_k^{(0)} \right) + \\
&\lambda^2 \left(\hat{H}^{(0)} \psi_k^{(2)} + \hat{H}^{(1)} \psi_k^{(1)} - E_k^{(0)} \psi_k^{(2)} - E_k^{(1)} \psi_k^{(1)} - E_k^{(2)} \psi_k^{(0)} \right) + \\
&\ldots = 0
\end{aligned}$$

4.162

The solution of the first of these equations (for λ^0) is known by assumption,

$$\hat{H}^{(0)} |k\rangle = E_k^{(0)} |k\rangle \qquad \text{where } |k\rangle \equiv \psi_k^{(0)}$$

To find $E_k^{(1)}$, we project the first-order correction of the wave function onto a complete orthonormal set of zero-order functions $\{|n\rangle\}$:

$$\psi_k^{(1)} = \sum_n a_n |n\rangle$$

The equation resulting from the vanishing of the λ^1 coefficient can then be written as:

$$\sum_n a_n (H^{(0)} - E_k^{(0)}) |n\rangle = (E_k^{(1)} - H^{(1)}) |k\rangle \tag{5}$$

4.163

Now we take the inner product of both sides of the equation with $|k\rangle$ (i.e., multiply from the left by $\langle k|$ and integrate):

$$\begin{aligned}
&\sum_n a_n \langle k| H^{(0)} - E_k^{(0)} |n\rangle = \langle k| (E_k^{(1)} - H^{(1)}) |k\rangle \\
&\underbrace{\sum_n a_n (E_n^{(0)} - E_k^{(0)}) \delta_{kn}}_{0} = E_k^{(1)} - \langle k| H^{(1)} |k\rangle \\
&E_k^{(1)} = \langle k| H^{(1)} |k\rangle \equiv H_{kk}^{(1)}
\end{aligned}$$

4.164

Let us now find the first-order correction to the wave function (i.e., the coefficients a_n in the expansion of $\psi_k^{(1)}$). As before, we multiply equation corresponding to λ^1 from the left by $\langle m|$ (this time with $m \neq k$) and integrate:

$$\sum_n a_n \langle m|H^{(0)} - E_k^{(0)}|n\rangle = \langle m|(E_k^{(1)} - H^{(1)})|k\rangle$$
$$\underbrace{\sum_n a_n (E_n^{(0)} - E_k^{(0)})\delta_{mn}}_{a_m(E_m^{(0)} - E_k^{(0)})} = E_k^{(1)}\delta_{mk} - \langle m|H^{(1)}|k\rangle$$

Only one term on the left is nonzero (for $m = n$) and the right-hand side reduces to the integral $H_{mk}^{(1)}$, so:

$$a_m = \frac{H_{mk}^{(1)}}{E_k^{(0)} - E_m^{(0)}} \rightsquigarrow \psi_k^{(1)} = \sum_{n\neq k} \frac{H_{mk}^{(1)}}{E_k^{(0)} - E_m^{(0)}}|n\rangle$$

4.165

Finding the second-order correction to energy $E_k^{(2)}$ is analogous to the first. The unknown second-order wave function correction is projected onto the complete orthonormal set of zero-order functions $\{|n\rangle\}$:

$$\psi_k^{(2)} = \sum_n b_n |n\rangle$$

The equation resulting from the vanishing of the λ^2 coefficient can be written as:

$$\sum_n b_n (H^{(0)} - E_k^{(0)})|n\rangle = (E_k^{(2)} - H^{(2)})|k\rangle + \sum_n a_n (E_k^{(1)} - H^{(1)})|n\rangle$$

4.166

As before, we "close" the equation on the left by multiplying with $\langle k|$ and integrating:

$$\sum_n b_n \langle k|H^{(0)} - E_k^{(0)}|n\rangle = \langle k|(E_k^{(2)} - H^{(2)})|k\rangle + \sum_n a_n \langle k|E_k^{(1)} - H^{(1)}|n\rangle$$
$$\underbrace{\sum_n b_n (E_n^{(0)} - E_k^{(0)})\delta_{kn}}_{0} = E_k^{(2)} - H_{kk}^{(2)} + \underbrace{\sum_n a_n (E_k^{(1)}\delta_{kn} - H_{kn}^{(1)})}_{\text{vanishes for } n=k}$$
$$E_k^{(2)} = H_{kk}^{(2)} + \sum_{n\neq k} a_n H_{kn}^{(1)}$$

4.167

We finally obtain the following expressions for the first corrections to energy and wave function:

$$E_k^{(1)} = \langle k|H^{(1)}|k\rangle \equiv H_{kk}^{(1)}$$
$$\psi_k^{(1)} = \sum_{n\neq k} \frac{H_{mk}^{(1)}}{E_k^{(0)} - E_m^{(0)}}|n\rangle$$
$$E_k^{(2)} = H_{kk}^{(2)} + \sum_{n\neq k} \frac{H_{nk}^{(1)} H_{kn}^{(1)}}{E_k^{(0)} - E_n^{(0)}}$$

4.168

Example 1
An electron confined in an infinite potential well of length L is subjected to a uniform electric field $\mathscr{E}$. The electron is thus subject to a force $-e\mathscr{E}$ and the potential between $x = 0$ and $x = L$ is $V = e\mathscr{E}x$. Find the ground state energy to first order in perturbation theory.

$$\hat{H} = \underbrace{\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}}_{\hat{H}^{(0)}} + \underbrace{e\mathscr{E}x}_{\hat{H}^{(1)}}$$

since: $E_n^{(0)} = \dfrac{n^2h^2}{8mL^2}$ and $\psi_n^{(0)} = \sqrt{\dfrac{2}{L}}\sin\left(\dfrac{n\pi}{L}x\right)$

$$E_n^{(1)} = \int_0^L \psi_n^{(0)}\hat{H}^{(1)}\psi_n^{(0)}\,dx = e\mathscr{E}\int_0^L \psi_n^{(0)} x \psi_n^{(0)}\,dx = e\mathscr{E}\langle x\rangle = \frac{e\mathscr{E}L}{2}$$

we find:

$$E_1 = E_1^{(0)} + E_1^{(1)} = \frac{h^2}{8mL^2} + \frac{e\mathscr{E}L}{2}$$

4.169

4.4 Determinantal Wave Function

Electronic Structure of the He Atom
Let us consider the electronic structure of the simplest two-electron system — the helium atom ($Z = 2$).
The electronic Hamiltonian is given by:

$$H^{el} = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}}_{h(\mathbf{r_1})} \underbrace{-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}}_{h(\mathbf{r_2})} + \frac{1}{|r_2 - r_1|}$$

where $h(\mathbf{r}_i) = h(i)$ is the one-electron Hamiltonian.

The analytical solution to the eigenvalue problem

$$H\psi(\mathbf{r}_1,\mathbf{r}_2) = E\psi(\mathbf{r}_1,\mathbf{r}_2)$$

is unknown due to the term $\frac{1}{|r_2-r_1|} = \frac{1}{r_{12}}$, which depends on the coordinates of both electrons. 4.170

If, however, we momentarily neglect the troublesome electron repulsion term in the Hamiltonian, the electronic Hamiltonian can be written as a *sum of non-interacting electron Hamiltonians*:

$$H^{el} \approx h(\mathbf{r_1}) + h(\mathbf{r_2})$$

If the Hamiltonian is written as a sum of independent terms, its eigenfunction can be expressed as a product:

$$\begin{aligned}(h(\mathbf{r_1}) + h(\mathbf{r_2}))\,\psi(\mathbf{r}_1,\mathbf{r}_2) &= (h(\mathbf{r_1}) + h(\mathbf{r_2}))\,\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \\ &= (E_1 + E_2)\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\end{aligned}$$

where

$$h(\mathbf{r_i})\psi_i(\mathbf{r}_i) = E_i\psi_i(\mathbf{r}_i)$$

is the eigenvalue problem for a hydrogen-like atom with known solutions.

4.171

Treating the electron repulsion as a perturbation in a degenerate two-state system,[1] the first-order energy correction of the system is:

$$E^{(1)} = \langle\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)|\frac{1}{r_{12}}|\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\rangle = J$$

Coulomb Integral

The term J is called the Coulomb integral, as it corresponds to the Coulomb repulsion potential of two discrete electron density distributions:

$$\begin{aligned}J &= \int \mathbf{dr}_1\,\mathbf{dr}_2\,|\psi_1(\mathbf{r}_1)|^2\frac{1}{|r_2-r_1|}|\psi_2(\mathbf{r}_2)|^2 \\ J &= \int \mathbf{dr}_1\,\mathbf{dr}_2\,\frac{\rho_1(\mathbf{r}_1)\rho_2(\mathbf{r}_2)}{|r_2-r_1|}\end{aligned}$$

4.172

The total ground-state energy of the helium atom, corresponding to the $1s^2$ electron configuration, is approximately:

$$E = E_1 + E_2 + J$$

The computed value of the Coulomb integral is $J = 2.50hc\mathscr{R}$, thus:

$$E = (-4-4+2.5)hc\mathscr{R} = 5.5hc\mathscr{R}$$

This value corresponds to -7220 kJmol^{-1} and, considering the approximations used, is fairly close to the experimentally determined sum of the first and second ionization potentials, which is -7619 kJmol^{-1}.[2] 4.173

[1] See perturbation theory

[2] The convergence condition for low-order perturbation theory requires the perturbation to be small — here the perturbation is quite large.

The situation becomes more complicated in the case of excited helium states with configuration $1s^1nl^1$. In this case, there are two possible wavefunctions for the non-interacting particle system:

$$\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \text{ and } \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1),$$

which we denote as:

$$\phi_1 = |a(1)b(2)\rangle \text{ and } \phi_2 = |a(2)b(1)\rangle.$$

Both wavefunctions correspond to the same eigenvalue $E_a + E_b$ (i.e., degenerate states). Applying perturbation theory in this case requires replacing the degenerate functions with mutually orthogonal linear combinations and solving the secular equation system:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

4.174

Since we chose mutually orthogonal linear combinations of the degenerate states, we have $S_{ij} = \delta_{ij}$, meaning $S_{11} = S_{22} = 1$ and $S_{12} = S_{21} = 0$.[1ex] We then obtain two different Hamiltonian matrix elements:

$$\begin{aligned} H_{11} &= \langle\phi_1|H|\phi_1\rangle = \langle a(1)b(2)|h(1) + h(2) + \frac{1}{r_{12}}|a(1)b(2)\rangle = \\ &= E_a + E_b + J = H_{22} \\ H_{12} &= \langle\phi_1|H|\phi_2\rangle = \langle a(1)b(2)|h(1) + h(2) + \frac{1}{r_{12}}|a(2)b(1)\rangle = \\ &= \langle a(1)b(2)|\frac{1}{r_{12}}|a(2)b(1)\rangle = H_{21} = K \end{aligned}$$

4.175

Exchange Integral

The integral K is referred to as the exchange integral, although it lacks a simple classical interpretation (it is a quantum mechanical correction to the Coulomb integral):

$$K = \int \mathbf{dr}_1\, \mathbf{dr}_2\, \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\frac{1}{|r_2 - r_1|}\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)$$

Solving the secular equation system:

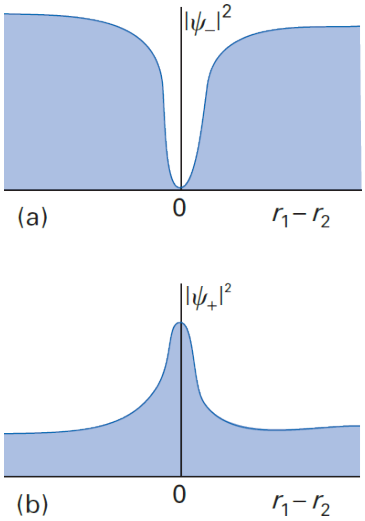
$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = \begin{vmatrix} E_a + E_b + J - E & K \\ K & E_a + E_b + J - E \end{vmatrix} = 0$$

leads to the following solutions:

$$\boxed{\begin{aligned} E_\pm &= E_a + E_b + J \pm K \\ \psi_\pm &= \frac{1}{\sqrt{2}}(a(1)b(2) \pm a(2)b(1)) \end{aligned}}$$

4.176

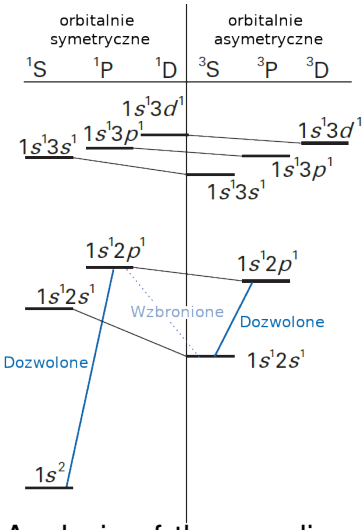
Fermi Hole and Fermi Heap



Electron
repulsion lifts the degeneracy of states, which now differ in energy by $\Delta E_{\pm} = 2K$.[1ex] However, the two solutions also differ dramatically as the distance between the electrons approaches zero. The probability density in the antisymmetric state ψ_- goes to zero for $\mathbf{r}_1 = \mathbf{r}_2$ (a), while in the symmetric state ψ_+ it paradoxically increases (b). This is the so-called *Fermi hole and Fermi heap*.

Since in the ψ_- state the electrons tend to avoid each other, their Coulomb repulsion is smaller $(J - K)$, and this effect is described by the exchange integral. In the ψ_+ state, we observe the opposite effect $(J + K)$. 4.177

Spectrum of Helium Atom States



The experimental
spectrum of electronic states is qualitatively consistent with these predictions. Antisymmetric states (from which transitions to the symmetric ground state are forbidden) lie lower than the corresponding symmetric terms. However, there is one more striking pattern — *all singlet states are symmetric, and all triplet states are antisymmetric*.

Analysis of the coupling electric dipole transition moment explains why transitions are only allowed between states of the same orbital symmetry:

$$\mu_{+-} = -\int \mathbf{dr}_1\, \mathbf{dr}_2\, \psi_+^*(\mathbf{r}_1, \mathbf{r}_2)(\mathbf{r}_1 + \mathbf{r}_2)\psi_-(\mathbf{r}_1, \mathbf{r}_2) = 0$$

4.178

Further analysis of the spectrum shows that only half of the possible states are realized. As it turns out, this is a consequence of a fundamental law of nature.

Pauli Exclusion Principle

Wolfgang Pauli observed that only those states are observed for which the total wavefunction (including electron spin) is antisymmetric with respect to the exchange of coordinates of any pair of electrons. As was later discovered, in fact:

*the wavefunction must be **symmetric** under exchange of a pair of identical **bosons**, and **antisymmetric** under exchange of a pair of identical **fermions**.*

4.179

In non-relativistic quantum mechanics, the Hamiltonian does not depend on spin coordinates, so the total wavefunction can be written as a product. For a two-electron system, one can construct 4 spin functions; one with total spin $S = 0$:

$$\sigma_-^{(0)}(\mathbf{s}_1, \mathbf{s}_2) = \frac{1}{\sqrt{2}}\left(\alpha(\mathbf{s}_1)\beta(\mathbf{s}_2) - \alpha(\mathbf{s}_2)\beta(\mathbf{s}_1)\right)$$

and three corresponding to three different values of the total spin projection in the triplet state ($S = 1$):

$$\begin{aligned}
\sigma_+^{(+1)}(\mathbf{s}_1, \mathbf{s}_2) &= \alpha(\mathbf{s}_1)\alpha(\mathbf{s}_2) \\
\sigma_+^{(0)}(\mathbf{s}_1, \mathbf{s}_2) &= \frac{1}{\sqrt{2}}\left(\alpha(\mathbf{s}_1)\beta(\mathbf{s}_2) + \alpha(\mathbf{s}_2)\beta(\mathbf{s}_1)\right) \\
\sigma_+^{(-1)}(\mathbf{s}_1, \mathbf{s}_2) &= \beta(\mathbf{s}_1)\beta(\mathbf{s}_2)
\end{aligned}$$

4.180

As it turns out, out of the eight possible combinations for the $1s^1np^1$ configuration, only four are experimentally observed — those for which the wavefunction is antisymmetric with respect to the exchange of the coordinates of an electron pair:

$\psi_-\sigma_-^{(0)}$	$\boxed{\psi_+\sigma_-^{(0)}}$	$\boxed{\psi_-\sigma_+^{(+1)}}$	$\psi_+\sigma_+^{(+1)}$
$\boxed{\psi_-\sigma_+^{(0)}}$	$\psi_+\sigma_+^{(0)}$	$\boxed{\psi_-\sigma_+^{(-1)}}$	$\psi_+\sigma_+^{(-1)}$

4.181

Slater Determinant
A wavefunction that is antisymmetric with respect to the permutation of a pair of electrons can be written in determinant form. For example, for the ground state of the helium atom:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = \psi_+(\mathbf{r}_1,\mathbf{r}_2)\sigma_-^{(0)}(\mathbf{s}_1,\mathbf{s}_2) = \\ = \chi_{1s}(\mathbf{r}_1)\chi_{1s}(\mathbf{r}_2)\frac{1}{\sqrt{2}}\left(\alpha(\mathbf{s}_1)\beta(\mathbf{s}_2)+\alpha(\mathbf{s}_2)\beta(\mathbf{s}_1)\right)$$

where $\mathbf{x}_i = (\mathbf{r}_i,\mathbf{s}_i)$ denotes the vector of spatial and spin coordinates of the i-th electron (usually it's enough to just write the index i).
After multiplying out, we find that there are only two distinct products of spatial and spin functions: $\phi_{1s}^{\alpha}(i) = \chi_{1s}(\mathbf{r}_i)\alpha(\mathbf{s}_i)$ and $\phi_{1s}^{\beta}(i) = \chi_{1s}(\mathbf{r}_i)\beta(\mathbf{s}_i)$. Thus, the wavefunction can be written in determinant form as:

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_{1s}^{\alpha}(1) & \phi_{1s}^{\alpha}(2)\\ \phi_{1s}^{\beta}(1) & \phi_{1s}^{\beta}(2)\end{vmatrix}$$

4.182

4.5 Hartree–Fock Method

In general, an antisymmetric wavefunction in the LCAO MO method can always be written in determinant form (although sometimes a linear combination is required). For an N-electron wavefunction, the Slater determinant in a basis of spin orbitals $\{\varphi_i\}$ is:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & \ldots & \varphi_1(\mathbf{x}_N)\\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & \ldots & \varphi_2(\mathbf{x}_N)\\ \cdots & \cdots & \cdots & \cdots\\ \varphi_N(\mathbf{x}_1) & \varphi_N(\mathbf{x}_2) & \ldots & \varphi_N(\mathbf{x}_N)\end{vmatrix}$$

or in short:

$$\Psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}}\det|\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)|$$

The orbital picture is very intuitive but cannot be exact for real systems because it relies on the one-electron approximation. However, within this approximation, we can find the best possible set of molecular orbitals.

4.183

A widely used method is the so-called *self-consistent field method* of Hartree–Fock. In this approach, we seek a variational solution to the eigenvalue problem using a determinantal wavefunction and the electronic Hamiltonian:

$$H = \sum_{i=1}^{N} h(i) + \sum_{j>i}^{N} r_{ij}^{-1}$$

where $h(i)$ is the one-electron Hamiltonian in an external potential $\upsilon(i)$:

$$h(i) = -\frac{1}{2}\nabla_i^2 + \upsilon(i)$$

4.184

Substituting H and Ψ into the energy functional $E[\Psi]$ gives:

$$E[\Psi] = \int \mathrm{d}\tau \Psi^* H \Psi = \\ = \frac{1}{N!} \int \mathrm{d}\tau \, |\varphi_1^*(1)\varphi_2^*(2)\cdots\varphi_N^*(N)|H|\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)|$$

Expanding the determinant on the left gives a linear combination of $N!$ terms differing by permutations of electrons. Each of these will yield the same result because the right-hand side includes all possible permutations. Therefore, we get $N!$ integrals of the type:

$$E[\Psi] = \int \mathrm{d}\tau \varphi_1^*(1)\varphi_2^*(2)\cdots\varphi_N^*(N)H|\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)|$$

where

$$\mathrm{d}\tau = \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N$$

and $\mathbf{x}_i$ is the space ($\mathbf{r}_i$) and spin ($\mathbf{s}_i$) coordinates of particle i.

4.185

Let's compute the contribution from $h(1)$. A nonzero result is obtained only when the same permutation appears on both sides, since spin orbitals are orthonormal. We thus get N integrals of the following form:

$$I_1 = \int \mathrm{d}\tau \, \varphi_1^*(1)\varphi_2^*(2)\cdots\varphi_N^*(N)h(1)|\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)|$$

$$\boxed{I_1 = \int \mathrm{d}\mathbf{x}_1 \varphi_1^*(1)h(1)\varphi_1(1)}$$

Considering a similar contribution from the r_{ij}^{-1} term, we get integrals of the form:

$$\int \mathrm{d}\tau \, \varphi_1^*(1)\varphi_2^*(2)\cdots\varphi_N^*(N)r_{ij}^{-1}\varphi_k(1)\varphi_l(2)\cdots\varphi_N(N)$$

4.186

Again, due to the orthonormality of spin orbitals, a nonzero result is obtained only for $k,l = 1,2$ and identical permutations of the remaining spin orbitals. This gives us two types of integrals: Coulomb integrals:

$$\boxed{J_{12} = \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \varphi_1^*(1)\varphi_2^*(2)r_{12}^{-1}\varphi_1(1)\varphi_2(2)}$$

and exchange integrals:

$$\boxed{-K_{12} = -\int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \varphi_1^*(1)\varphi_2^*(2)r_{12}^{-1}\varphi_1(2)\varphi_2(1)}$$

Since each r_{ij}^{-1} term gives one pair of integrals J_{ij} and K_{ij}, their total contribution to the electronic energy is:

$$\sum_{i=1}^{N}\sum_{j>i}^{N}(J_{ij}-K_{ij}) = \frac{1}{2}\sum_{i,j}^{N}(J_{ij}-K_{ij}) = \sum_{i=2}^{N}\sum_{j=1}^{i-1}(J_{ij}-K_{ij})$$

4.187

Ultimately, the electronic energy for a determinantal wavefunction is:

$$\boxed{E[\Psi] = \sum_{i=1}^{N} I_i + \frac{1}{2}\sum_{i,j}^{N}(J_{ij} - K_{ij})}$$

To find the optimal form of the spin orbitals, we calculate the variation δE caused by varying the orbitals and set it to zero:

$$\delta E[\Psi] = \sum_{i=1}^{N} \delta I_i + \frac{1}{2}\sum_{i,j}^{N}(\delta J_{ij} - \delta K_{ij}) = 0$$

The changes in orbitals are essentially arbitrary, but must preserve their orthogonality:

$$S_{ij} = \int \mathrm{d}\mathbf{x}_1 \varphi_i^*(1)\varphi_j(1) = \delta_{ij} \quad \text{for} \quad i,j = 1,2,\ldots,N$$

4.188

These additional constraints can be incorporated using the method of Lagrange multipliers ε_{ij}:

$$\varepsilon_{ij}(S_{ij} - \delta_{ij}) = 0 \quad \text{for} \quad i,j = 1,2,\ldots,N$$

If these conditions are met, then:

$$E[\Psi] = \sum_{i=1}^{N} I_i + \frac{1}{2}\sum_{i,j}^{N}(J_{ij} - K_{ij}) - \sum_{i,j}^{N}\varepsilon_{ij}(S_{ij} - \delta_{ij})$$

$$\delta E[\Psi] = \sum_{i=1}^{N} \delta I_i + \frac{1}{2}\sum_{i,j}^{N}(\delta J_{ij} - \delta K_{ij}) - \sum_{i,j}^{N}\varepsilon_{ij}\delta S_{ij} \tag{6}$$

For real orbitals:

$$\begin{aligned}\delta I_i &= \delta \int \mathrm{d}\mathbf{x}_1\, \varphi_i(1)h(1)\varphi_i(1) = \\ &= \int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)]h(1)\varphi_i(1) + \int \mathrm{d}\mathbf{x}_1\, \varphi_i(1)h(1)[\delta\varphi_i(1)] = \\ &= 2\int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)]h(1)\varphi_i(1)\end{aligned} \tag{7}$$

4.189

For the variation of overlap integrals, we get two different terms but their sum is identical:

$$\begin{aligned}\delta S_{ij} &= \delta \int \mathrm{d}\mathbf{x}_1\, \varphi_i(1)\varphi_j(1) = \\ &= \int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)]\varphi_j(1) + \int \mathrm{d}\mathbf{x}_1\, \varphi_i(1)[\delta\varphi_j(1)]\end{aligned} \tag{8}$$

To consider the variation of two-electron integrals, it is useful to introduce two Hermitian operators: the Coulomb and exchange operators, defined by their action on spin orbitals:

$$\boxed{\begin{aligned}\hat{\mathscr{J}}_i(1)\varphi_k(1) &= \left[\int \mathrm{d}\mathbf{x}_2\, \varphi_i(2)r_{12}^{-1}\varphi_i(2)\right]\varphi_k(1) \\ \hat{\mathscr{K}}_i(1)\varphi_k(1) &= \left[\int \mathrm{d}\mathbf{x}_2\, \varphi_i(2)r_{12}^{-1}\varphi_k(2)\right]\varphi_i(1)\end{aligned}}$$

4.190

The Coulomb and exchange integrals can now be expressed using the respective operators:

$$J_{ij} = \int \mathrm{d}\mathbf{x}_1\, \varphi_i(1)\, \hat{\mathscr{J}}_j(1)\varphi_i(1) = \int \mathrm{d}\mathbf{x}_2\, \varphi_j(2)\, \hat{\mathscr{J}}_i(2)\varphi_j(2)$$
$$K_{ij} = \int \mathrm{d}\mathbf{x}_1\, \varphi_i(1)\hat{\mathscr{K}}_j(1)\varphi_i(1) = \int \mathrm{d}\mathbf{x}_2\, \varphi_j(2)\hat{\mathscr{K}}_i(2)\varphi_j(2)$$

When considering the variation of φ_i, we conventionally use the first definition, and for φ_j, the second:

$$\delta J_{ij} = 2\int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)]\, \hat{\mathscr{J}}_j(1)\varphi_i(1) + 2\int \mathrm{d}\mathbf{x}_2\, [\delta\varphi_j(2)]\, \hat{\mathscr{J}}_i(2)\varphi_j(2)$$
$$\delta K_{ij} = 2\int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)].\hat{\mathscr{K}}_j(1)\varphi_i(1) + 2\int \mathrm{d}\mathbf{x}_2\, [\delta\varphi_j(2)].\hat{\mathscr{K}}_i(2)\varphi_j(2)$$

4.191

Substituting the expressions for the variation of one- and two-electron integrals into equation (6) yields:

$$\begin{aligned}\delta E[\Psi] = 2\sum_{i=1}^{N}\int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)]h(1)\varphi_i(1) + \\ + \sum_{i,j}^{N}\Bigg(2\int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)]\, \hat{\mathscr{J}}_j(1)\varphi_i(1) - \\ - 2\int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)].\hat{\mathscr{K}}_j(1)\varphi_i(1)\Bigg) - \\ - \sum_{i,j}^{N}\varepsilon_{ij}\left(\int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)]\varphi_j(1) + \int \mathrm{d}\mathbf{x}_1\, \varphi_i(1)[\delta\varphi_j(1)]\right)\end{aligned}$$

4.192

Which simplifies to:

$$\begin{aligned}\delta E[\Psi] = 2\sum_{i=1}^{N}\int \mathrm{d}\mathbf{x}_1\, [\delta\varphi_i(1)]\Bigg\{h(1)\varphi_i(1) + \\ + \sum_{j=1}^{N}\left(\hat{\mathscr{J}}_j(1)\varphi_i(1) - \hat{\mathscr{K}}_j(1)\varphi_i(1) - \varepsilon_{ij}\varphi_j(1)\right)\Bigg\} = 0\end{aligned}$$

Since $\delta\varphi_i$ are arbitrary, this equation is satisfied only if the coefficients of $\delta\varphi_i$ vanish identically:

$$\underbrace{\left\{h(1) + \sum_{j=1}^{N}\left(\hat{\mathscr{J}}_j(1) - \hat{\mathscr{K}}_j(1)\right)\right\}}_{\hat{\mathscr{F}}(1)=\hat{h}(1)+\hat{\mathscr{J}}(1)-\hat{\mathscr{K}}(1)}\varphi_i(1) = \sum_{j=1}^{N}\varepsilon_{ij}\varphi_j(1)$$

where we introduce the *Fock operator* $\hat{\mathscr{F}}$.

4.193

Since a unitary transformation does not change the Slater determinant, the determinantal wavefunction is defined up to a unitary transformation

(thus infinitely many wavefunctions exist with the same energy eigenvalue). Because the Lagrange multipliers form a Hermitian matrix, it can be diagonalized with an appropriate unitary transformation. Then:

$$\varepsilon_{ii} = \varepsilon_i \qquad \text{and} \quad \varepsilon_{ij} = 0$$

The resulting integro-differential equation system:

$$\mathscr{F}(1)\varphi_i(1) = \sum_{j=1}^{N} \varepsilon_{ij}\varphi_j(1)$$

simplifies to:

$$\boxed{\mathscr{F}(1)\varphi_i(1) = \varepsilon_i\varphi_i(1) \quad \text{for} \quad i = 1,2,\ldots,N} \tag{4.194}$$

Hartree–Fock Roothaan Method

The SCF method requires solving a system of integro-differential equations at each step of the iterative procedure. This is a nontrivial task and is difficult to carry out directly in practice. Therefore, an additional approximation is introduced in which molecular orbitals are expanded in a finite set of known basis functions.

$$\varphi_i(\mathbf{x}) = \sum_{r=1}^{M} c_{ri}\,\chi_r(\mathbf{x})$$

where basis functions $\{\chi_r\}$ are typically atomic-type orbitals. If M basis functions are used, one obtains M linearly independent combinations, and therefore M spin-orbitals. The task is thus reduced to determining the coefficients c_{ri} that minimize the total energy. (4.195)

Algebraic Form of the Equations

Substituting the expansion of the spin-orbitals into the Hartree–Fock equations leads to a system of algebraic equations:

$$\mathbb{F}\mathbb{C} = \mathbb{S}\mathbb{C}\mathbb{E}$$

Here, $\mathbb{C}$ is the matrix of expansion coefficients, where each column corresponds to a given spinorbital, and $\mathbb{E}$ is the diagonal matrix of orbital energies $\{\varepsilon_i\}$.

For each spin-orbital, the equation can be written in vector form as:

$$\mathbb{F}\,\mathbf{c}_i = \varepsilon_i\,\mathbb{S}\,\mathbf{c}_i$$

where

$$\mathbb{C} = \begin{bmatrix}\mathbf{c}_1 & \mathbf{c}_2 & \cdots & \mathbf{c}_M\end{bmatrix} \qquad \mathbf{c}_i = \begin{bmatrix} c_{1i} \\ c_{2i} \\ \vdots \\ c_{Mi} \end{bmatrix} \tag{4.196}$$

Fock Matrix Elements for RHF

The matrix $\mathbb{F}$ is the Fock matrix expressed in the basis $\{\chi_r\}$ and contains one-electron and two-electron contributions:

$$F_{rs} = \langle \chi_r | \hat{f} | \chi_s \rangle = h_{rs} + \sum_{tu} P_{tu} \left[(rs|tu) - \tfrac{1}{2}(rt|su) \right]$$

where h_{rs} are the one-electron matrix elements, and the two-electron integrals in chemist notation are

$$(rs|tu) = \iint \chi_r^*(x_1)\chi_s(x_1) \frac{1}{r_{12}} \chi_t^*(x_2)\chi_u(x_2)\, dx_1 dx_2$$

and P is the density matrix given by

$$P_{rs} = 2\sum_{i}^{\text{occ}} c_{ri} c_{si}$$

It depends on occupied orbitals and couples equations, thus requires self-consistency.

4.197

Orthogonalization of the Roothaan Equations

The Roothaan equations form a generalized eigenvalue problem:

$$\mathbb{FC} = \mathbb{SCE}$$

Since $\mathbb{S} \neq \mathbb{I}$, we transform to an orthonormal basis. Let $\mathbb{X}$ satisfy

$$\mathbb{X}^\top \mathbb{S} \mathbb{X} = \mathbb{I}.$$

A common choice is the symmetric orthogonalization $\mathbb{X} = \mathbb{S}^{-1/2}$. The problem is then transformed to an ordinary Hermitian eigenvalue problem in an orthonormal basis:

$$\mathbb{FC} = \mathbb{SCE} \rightsquigarrow \mathbb{F}'\mathbb{C}' = \mathbb{C}'\mathbb{E}$$

where

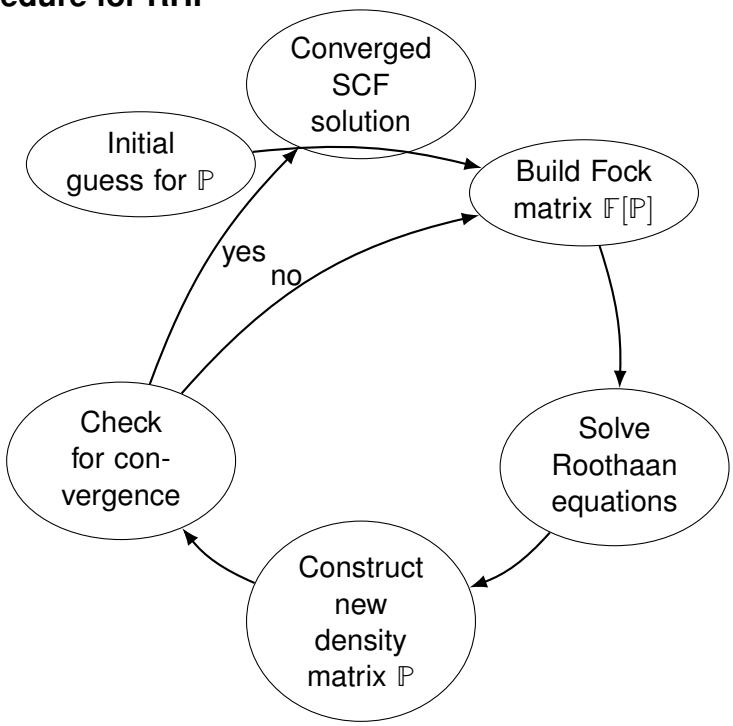
$$\mathbb{F}' = \mathbb{X}^\top \mathbb{F} \mathbb{X}, \qquad \mathbb{C}' = \mathbb{X}^{-1}\mathbb{C}.$$

After solving for $\mathbb{C}'$, the AO-basis coefficients are recovered via back transformation:

$$\mathbb{C} = \mathbb{X}\mathbb{C}'$$

4.198

SCF Procedure for RHF



4.199

4.6 Molecular Orbitals

From perturbation theory in a two-level system, it follows that in the case of close or degenerate atomic orbital energy levels, a *splitting* occurs:

$$\begin{vmatrix} \alpha_{\mathrm{A}} - E & \beta - ES \\ \beta - ES & \alpha_{\mathrm{B}} - E \end{vmatrix} = 0$$

$$E_{\pm} = \frac{\alpha_{\mathrm{A}} + \alpha_{\mathrm{B}}}{2} \pm \frac{\sqrt{(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})^2 + 4\beta^2}}{2}$$

(for $S \approx 0$), which can be written as:

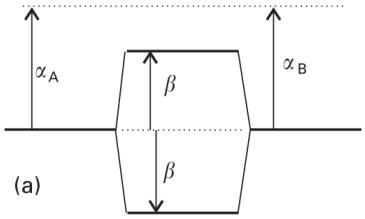
$$E_{\pm} = \frac{\alpha_{\mathrm{A}} + \alpha_{\mathrm{B}}}{2} \pm \frac{\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}}{2} \sqrt{1 + \frac{4\beta^2}{(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})^2}}$$

For $\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}} \gg \beta$, using $\sqrt{1+x} \approx 1 + \frac{1}{2}x$:

$$E_{\pm} = \frac{\alpha_{\mathrm{A}} + \alpha_{\mathrm{B}}}{2} \pm \frac{\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}}{2} \left(1 + \frac{2\beta^2}{(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})^2}\right)$$

4.200

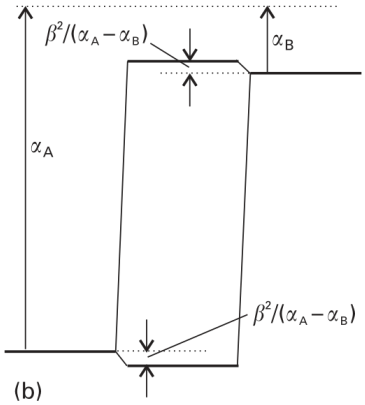
Molecular Orbital Energies



In the
case of degenerate atomic orbital energies:

$$E_{\pm} = \alpha_{A(B)} \pm \beta$$

and otherwise:

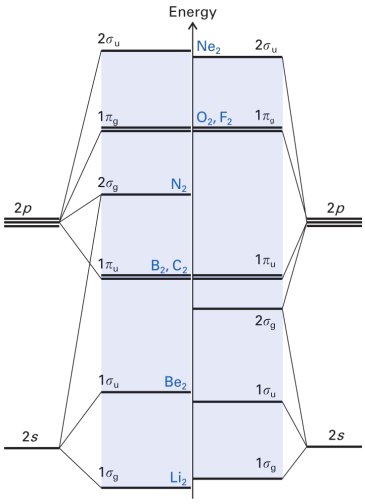


$$E_{+} = \alpha_A + \frac{\beta^2}{(\alpha_A - \alpha_B)}$$

$$E_{-} = \alpha_B - \frac{\beta^2}{(\alpha_A - \alpha_B)}$$

4.201

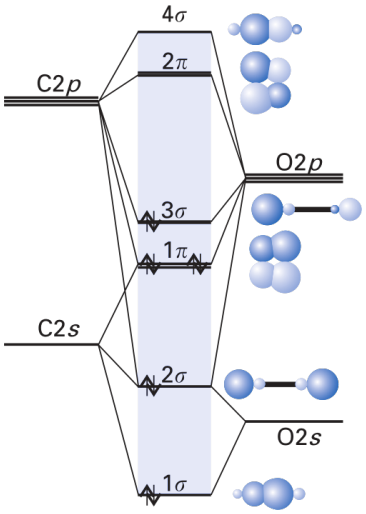
MO Diagram for Homonuclear Molecules



Energy levels
of molecular orbitals for diatomic molecules of second-period elements. Labels indicate the highest occupied level for each molecule. Due to s–p orbital mixing, the order of $2\sigma_g$ and π_u orbitals switches between N_2 and O_2.

4.202

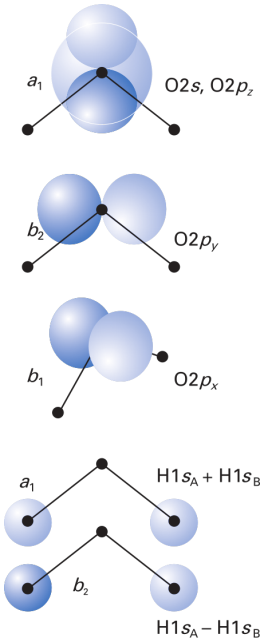
MO Diagram for Heteronuclear Molecules



Molecular
orbital diagram for the CO molecule.

4.203

MO Diagram for Polyatomic Molecules



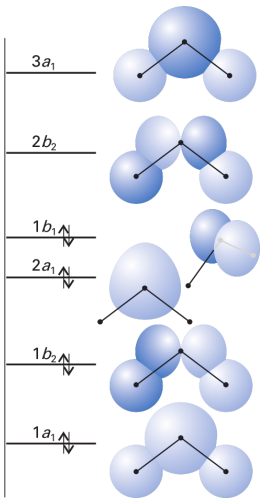
Character table for point group

C_2V

C_{2v}, $2mm$	E	C_2	σ_v	σ_v'	$h=4$	
A_1	1	1	1	1	z, z^2, x^2, y^2	
A_2	1	1	−1	−1	xy	R_z
B_1	1	−1	1	−1	x, xz	R_y
B_2	2	−1	−1	1	y, yz	R_x

4.204

MO Diagram for Polyatomic Molecules



Molecular orbital diagram for water
(H_2O), constructed using symmetry-adapted linear
combinations (SALCs) and the C_2V character table.

C_{2v}, $2mm$	E	C_2	σ_v	σ_v'	$h=4$	
A_1	1	1	1	1	z, z^2, x^2, y^2	
A_2	1	1	−1	−1	xy	R_z
B_1	1	−1	1	−1	x, xz	R_y
B_2	2	−1	−1	1	y, yz	R_x

4.205

4.7 Configuration Interaction

Correlation Energy

Definition of correlation energy according to Löwdin:

$$E_{\text{corr}} = E_{\text{exact}} - E_{HF}$$

Since E_{HF} is an upper bound to E_{exact}, the correlation energy is negative.
Hartree–Fock theory recovers **99%** of the energy, but... **the remaining 1% is extremely important in chemistry.**
Three main methods for calculating electron correlation:

- Configuration Interaction (CI) method
- Many-Body Perturbation Theory (MBPT)
- Coupled Cluster (CC) theory

4.206

Partitioning of the electronic energy of the Ne atom

The total energy can be represented as the sum of kinetic energy, interaction with the external potential (from point charges of atomic nuclei, etc.), electron–electron interaction energy in the self-consistent field approximation (classical and exchange), and the electron correlation energy.

$$E_e = T_e + V_{ne} + J_{ee} - K_{ee} + E_{\text{corr}}$$

For the Ne atom, these contributions are:

$$T_e = +129\,Eh$$
$$V_{ne} = -312\,Eh$$
$$J_{ee} = +66\,Eh$$
$$K_{ee} = -12\,Eh\ (9.3\%)$$
$$E_{\text{corr}} = -0.4\,Eh\ (0.3\%)$$

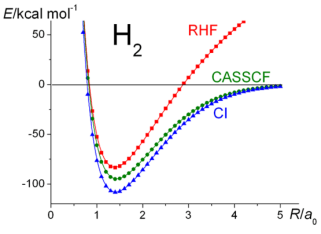
Thus, the Hartree–Fock energy constitutes 99% of the total energy. Can E_{corr} be neglected?

4.207

Dynamic vs Non-Dynamic Correlation

- **Dynamic**: electron avoidance (short-range)
- **Non-dynamic**: quasi-degeneracies, static effects

Stretched H_2 molecule



At equilibrium, the contribution of correlation is about 23.0%. CASSCF with two active molecular orbitals gives a qualitatively correct potential energy curve and recovers 53.4% of the correlation energy.[a]

[a] Bacskay *Molecules* 2025, 30(5), 1154

4.208

Conventions and Notation

Level	Symbol	Name	Alternative
1	S	single	single excitations
2	D	double	double excitations
3	T	triple	triple excitations
4	Q	quadruple	quadruple excitations

- $i, j, k, \ldots$: indices of occupied orbitals (holes)
- $a, b, c, \ldots$: virtual orbitals (unoccupied) (particles)
- $p, q, r, \ldots$: general orbitals
- ϕ or φ – (spin)orbitals
- Φ_0 or Ψ_0 or $|0\rangle$ – wavefunctions (in this case, the ground state)

4.209

Configuration Interaction

Matrix mechanics is easily implemented and naturally suits computers. It requires that we choose a vector space for the expansion of the problem. N-electron wavefunction requires N-particle functions. Assume that we have a complete set of functions $\chi_i(x_1)$ of a single variable x_1. Then any arbitrary function of that variable can be expanded exactly as:

$$\Phi(x_1) = \sum_i a_i \chi_i(x_1)$$

For two variables that have the same domain:

$$\Phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1)$$

for fixed x_2. We can now expand the coefficient $a_i(x_2)$

$$a_i(x_2) = \sum_j b_{ij} \chi_j(x_2)$$

what leads to

$$\Phi(x_1, x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2)$$

4.210

Antisymmetry and Slater Determinants

This procedure can be easily extended for $\Phi(x_1, x_2, \ldots, x_N)$. Here x represents both spin and space coordinates.

$$\Phi(x_1, x_2, \ldots, x_N) = \sum_{ij\ldots N} b_{ij\ldots N} \chi_i(x_1) \chi_j(x_2) \cdots \chi_N(x_N)$$

However, the wavefunction must be antisymmetric with respect to the exchange of the coordinates of any two electrons. Thus for two-particle case:

$$\Phi(x_1, x_2) = -\Phi(x_2, x_1)$$

what implies $b_{ij} = -b_{ji}$ and $b_{ii} = 0$:

$$\Phi(x_1, x_2) = \sum_{j>i} b_{ij} \left[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2) \right] = \\ = \sum_{j>i} \sqrt{2}\, b_{ij} \, |\chi_i \chi_j\rangle$$

4.211

Antisymmetry and Slater Determinants

More generally, an arbitrary N-electron wavefunction can be expressed exactly as a linear combination of all possible N-electron Slater determinants formed from a complete set of spin orbitals $\{\chi_i(x_1)\}$. If we solve the matrix mechanics problem $H|\Psi\rangle = E\Psi\rangle$ in a complete basis of N-electron functions, we will obtain all electronic eigenstates of the system exactly as the eigenvectors of $\mathbf{H}$

$$|\Psi_j\rangle = \sum_i c_{ij} |\Phi_i\rangle$$

The matrix elements $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$ may be put in terms of one- and two-electron integrals according to "Slater's rules". 4.212

CI Expansion from HF Reference

The N-electron basis functions $|\Phi_i\rangle$ can be written as substitutions or "excitations" from the Hartree-Fock "reference" determinant:

$$|\Psi\rangle = \underbrace{\underbrace{c_0 \underbrace{|\Phi_0\rangle}_{HF} + \sum_{ra} c_r^a |\Phi_a^r\rangle}_{CIS} + \sum_{a<b, r<s} c_{ab}^{rs} |\Phi_{ab}^{rs}\rangle}_{CISD} \\ + \sum_{r<s<t, a<b<c} c_{abc}^{rst} |\Phi_{abc}^{rst}\rangle + \ldots$$

4.213

Slater-Condon Rules

The one-electron and two-electron integrals in terms of spin-orbitals using physicist's notation are, respectively:

$$\langle i|\hat{h}|j\rangle = \int \phi_i^*(x_1) \hat{h}(x_1) \phi_j(x_1)\, dx_1$$
$$\langle ij||kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle \quad \text{where}$$
$$\langle ij|kl\rangle = \int \phi_i^*(x_1)\phi_j^*(x_2) \frac{1}{r_{12}} \phi_k(x_1)\phi_l(x_2)\, dx_1 dx_2$$

4.214

Slater-Condon Rules

- If the determinants are identical, then

$$\langle \Phi_1 | \hat{H} | \Phi_1 \rangle = \sum_m \langle m|h|m\rangle + \sum_{m>n} \langle mn||mn\rangle$$

- Determinants that Differ by One Spin Orbital:

$$\begin{aligned}|\Phi_1\rangle &= |\cdots mn\cdots\rangle \\ |\Phi_2\rangle &= |\cdots pn\cdots\rangle \\ \langle\Phi_1|\hat{H}|\Phi_2\rangle &= \langle m|h|p\rangle + \sum_n \langle mn||pn\rangle\end{aligned}$$

- Determinants that Differ by Two Spin Orbitals:

$$\begin{aligned}|\Phi_1\rangle &= |\cdots mn\cdots\rangle \\ |\Phi_2\rangle &= |\cdots pq\cdots\rangle \\ \langle\Phi_1|\hat{H}|\Phi_2\rangle &= \langle mn||pq\rangle\end{aligned}$$

- Determinants that differ by More than Two Spin Orbitals:

$$\langle\Phi_1|\hat{H}|\Phi_2\rangle = 0$$

4.215

Linear Variation Ansatz
Let us apply the method of linear variations for the CI wavefunction:

$$|\Psi\rangle = \sum_i c_i|\Phi_i\rangle$$

where $|\Phi_i\rangle$ are determinants. We vary the coefficients c_i to minimize the functional $E[\Psi]$ under the normalization constraint. We apply the method of Lagrange multipliers:

$$\mathscr{L} = \langle\Psi|\hat{H}|\Psi\rangle - E(\langle\Psi|\Psi\rangle - 1)$$

After substituting the CI expansion:

$$\mathscr{L} = \sum_{ij} c_i^* c_j H_{ij} - E\left(\sum_{ij} c_i^* c_j S_{ij} - 1\right)$$

where:

$$H_{ij} = \langle\Phi_i|\hat{H}|\Phi_j\rangle, \quad S_{ij} = \langle\Phi_i|\Phi_j\rangle$$

4.216

Stationarity Condition
We set the first variation of $\mathscr{L}$ to zero:

$$\begin{aligned}\delta\mathscr{L} = &\sum_{ij} \delta c_i^* c_j H_{ij} - E\sum_{ij} \delta c_i^* c_j S_{ij} \\ &+ \sum_{ij} c_i^* \delta c_j H_{ij} - E\sum_{ij} c_i^* \delta c_j S_{ij} = 0\end{aligned}$$

since $H_{ij} = H_{ji}^*$ and $S_{ij} = S_{ji}^*$, this gives:

$$\delta\mathscr{L} = \sum_i \delta c_i^* \left[\sum_j (H_{ij} - ES_{ij})c_j\right] + \text{c.c.} = 0$$

Each term is a sum of a number and its complex conjugate, so imaginary parts cancel. Since variation of the coefficients is arbitrary, the term in brackets must vanish. 4.217

Matrix Form of the Schrödinger Equation
This leads to an eigenvalue problem:

$$\mathbb{HC} = \mathbb{SCE}$$

If the basis functions $\{|\Phi_i\rangle\}$ are orthonormal, then $\mathbb{S} = \mathbb{I}$, where $\mathbb{C}$ is the vector of coefficients of $|\Psi\rangle$ in the basis $\{|\Phi_i\rangle\}$. Thus CI may be viewed as either:

- matrix form of the Schrödinger equation or
- variational minimization of energy with respect to c_i.

The variational method gives the best estimate of the energy in a given basis. 4.218

Application to Excited States
If $|\Psi\rangle$ is normalized, substituting the expansion over exact eigenfunctions gives:

$$E = \sum_i c_i^* c_i \varepsilon_i$$

where ε_i are exact energy eigenvalues. Subtracting the ground state energy:

$$E - \varepsilon_0 = \sum_i c_i^* c_i (\varepsilon_i - \varepsilon_0)$$

since $|\Psi\rangle$ is normalized and $\sum_i c_i^* c_i = 1$, which gives the bound $E \geq \varepsilon_0$.
In the case of excited states we may set the first k coefficients to zero and subtract ε_k from the top equation. If $c_j = 0$ for $j = 0, 1, \ldots, k$ this simplifies to:

$$E - \varepsilon_k = \sum_{i=k} c_i^* c_i (\varepsilon_i - \varepsilon_k) \geq 0$$

4.219

4.8 Møller–Plesset Partitioning

Møller–Plesset Partitioning
Another approach to improve the Hartree–Fock energy for an N-electron system is to use perturbation theory. We can partition the electronic Hamiltonian:

$$\mathscr{H} = \sum_i h(i) + \sum_{i<j} r_{ij}^{-1} = \mathscr{H}^{(0)} + \mathscr{V}$$

into the Hartree–Fock Hamiltonian $\mathscr{H}^{(0)}$ and $\mathscr{V}$ — the fluctuation operator (perturbation):

$$\mathscr{H}^{(0)} = \sum_i f(i) = \sum_i \left(h(i) + \upsilon^{HF}(i) \right)$$
$$\mathscr{V} = \mathscr{H} - \mathscr{H}^{(0)} = \sum_{i<j} r_{ij}^{-1} - \sum_i \upsilon^{HF}(i)$$

4.220

Two-electron Integrals
Assuming physicist's notation for two-electron integrals in the spin-orbital basis:

$$\langle ij|kl\rangle = \int dx_1 dx_2 \phi_i(x_1)^* \phi_j(x_2)^* r_{12}^{-1} \phi_k(x_1)\phi_l(x_2)$$
$$\langle ij||kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle$$

we obtain (a,b are occupied and r,s unocuppied MOs):

$$\langle \Psi_0| \sum_{i<j} r_{ij}^{-1} |\Psi_{ab}^{rs}\rangle = \langle ab||rs\rangle$$

and

$$\upsilon^{HF}(x_1)\phi_j(x_1) = \sum_b \langle b|r_{12}^{-1}|b\rangle \phi_j(x_1) - \sum_b \langle b|r_{12}^{-1}|j\rangle \phi_b(x_1)$$

consequently

$$\langle i|\upsilon^{HF}|j\rangle = \upsilon_{ij}^{HF} = \sum_b \langle ib|jb\rangle - \langle ib|bj\rangle = \sum_b \langle ib||jb\rangle$$

4.221

First-order Energy
The Hartree–Fock wavefunction $|\Psi_0\rangle$ is an eigenfunction of the operator $\mathscr{H}^{(0)}$:

$$\mathscr{H}^{(0)}|\Psi_0\rangle = E_0^{(0)}|\Psi_0\rangle$$

with eigenvalue:

$$E_0^{(0)} = \sum_a \varepsilon_a$$

which is the zeroth-order energy. The first-order energy is:

$$\begin{aligned} E_0^{(1)} &= \langle \Psi_0|\mathscr{V}|\Psi_0\rangle \\ &= \langle \Psi_0| \sum_{i<j} r_{ij}^{-1} |\Psi_0\rangle - \langle \Psi_0| \sum_i \upsilon^{HF}(i)|\Psi_0\rangle \\ &= \frac{1}{2}\sum_{ab} \langle ab||ab\rangle - \sum_a \langle a|\upsilon^{HF}|a\rangle \\ &= -\frac{1}{2}\sum_{ab} \langle ab||ab\rangle \end{aligned}$$

4.222

Second-order Energy
The Hartree–Fock energy is the sum of zeroth- and first-order energies:

$$E_0^{\mathrm{HF}} = E_0^{(0)} + E_0^{(1)} = \sum_a \varepsilon_a - \frac{1}{2}\sum_{ab} \langle ab||ab\rangle$$

The first correction due to electron correlation appears in second-order perturbation theory:

$$E_0^{(2)} = \sum_{n\neq 0} \frac{|\langle 0|\mathscr{V}|n\rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

Here $|0\rangle = |\Psi_0\rangle$, and the question remains which excitations $|n\rangle$ are allowed. They cannot be single excitations because:

$$\begin{aligned}\langle\Psi_0|\mathscr{V}|\Psi_a^r\rangle &= \langle\Psi_0|\mathscr{H}-\mathscr{H}^{(0)}|\Psi_a^r\rangle \\ &= \langle\Psi_0|\mathscr{H}|\Psi_a^r\rangle - f_{ar}\end{aligned}$$

where the first term vanishes by Brillouin's theorem, and the second because spin-orbitals are eigenfunctions of the Fock operator. 4.223

Taking into account the Slater–Condon rules, only double excitations remain. Since:

$$\mathscr{H}^{(0)}|\Psi_{ab}^{rs}\rangle = \left(E_0^{(0)} - (\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s)\right)|\Psi_{ab}^{rs}\rangle$$

the second-order energy is:

$$E_0^{(2)} = \sum_{\substack{a<b\\r<s}} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

or, since terms are symmetric with respect to a,b and r,s, and vanish when $a=b$ or $r=s$:

$$E_0^{(2)} = \frac{1}{4}\sum_{abrs} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

4.224

In terms of ordinary two-electron integrals:

$$E_0^{(2)} = \frac{1}{2}\sum_{abrs} \frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \frac{1}{2}\sum_{abrs} \frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

For a closed-shell system, this can be written in the spatial orbital basis:

$$E_0^{(2)} = 2\sum_{abrs}^{N/2} \frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \sum_{abrs}^{N/2} \frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$$

4.225

H_2 molecule in a minimal basis

$$\begin{aligned}E_0^{(2)} &= 2\frac{\langle 11|22\rangle\langle 22|11\rangle}{2(\varepsilon_1-\varepsilon_2)} - \frac{\langle 11|22\rangle\langle 22|11\rangle}{2(\varepsilon_1-\varepsilon_2)} \\ &= \frac{|\langle 11|22\rangle|^2}{2(\varepsilon_1-\varepsilon_2)} = \frac{K_{12}^2}{2(\varepsilon_1-\varepsilon_2)}\end{aligned}$$

It can be shown that for an H_2 oligomer:

$$E_0^{(2)} = \sum_{i=1}^{N-mers} \frac{|\langle\Psi_0|\mathscr{V}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle|^2}{2(\varepsilon_1-\varepsilon_2)} = \frac{NK_{12}^2}{2(\varepsilon_1-\varepsilon_2)}$$

4.226

Summary: Key MP2 Equations
We begin from the Hartree–Fock reference, where the molecular orbitals satisfy the Fock eigenvalue equation $\hat{f}\phi_a = \varepsilon_a\phi_a$. $E^{(0)}$ is thus a sum of orbital energies, and first-order correction retrieves HF energy:

$$E_0^{\mathrm{HF}} = E_0^{(0)} + E_0^{(1)} = \sum_a \varepsilon_a - \frac{1}{2}\sum_{ab}\langle ab||ab\rangle$$

To evaluate electron correlation, two-electron integrals must be expressed in the molecular orbital basis. This is achieved via the transformation from atomic orbitals:

$$\langle ab|rs\rangle = \sum_{\mu\nu\lambda\sigma} c_{\mu a}c_{\nu b}c_{\lambda r}c_{\sigma s}\langle\mu\nu|\lambda\sigma\rangle.$$

The second-order correction to the energy (MP2) is the first accounting for correlation energy:

$$E^{\mathrm{MP2}} = \sum_{a,b}^{\mathrm{occ}}\sum_{r,s}^{\mathrm{virt}} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

where $\langle ab||rs\rangle = \langle ab|rs\rangle - \langle ab|sr\rangle = (ar|bs) - (as|br)$ 4.227

4.9 Coupled clusters

Extensivity and size consistency
Size-consistent:

- Total energy of non-interacting systems:

$$E(AB) = E(A) + E(B)$$

Size-extensive:[3]

- Energy scales linearly with system size. Example for the helium dimer:

$$E(N\mathrm{He}) = NE(\mathrm{He})$$

4.228

Exponential ansatz
In CC theory it is assumed that the ground-state wavefunction $|\Psi_0\rangle$ has the form:

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle = \left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots\right)|\Phi_0\rangle$$

where $|\Phi_0\rangle$ is the reference function (usually Hartree-Fock), and $\hat{T}$ is the cluster operator:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$$

[3] implies size consistency (but not vice versa)

$$\hat{T}_1|\Phi_0\rangle = \sum_{i,a} t_i^a |\Phi_i^a\rangle$$
$$\hat{T}_2|\Phi_0\rangle = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$
$$\hat{T}_2^2|\Phi_0\rangle = \sum_{\substack{i>j \\ a>b}} \sum_{\substack{k>l \\ c>d}} t_{ij}^{ab} t_{kl}^{cd} |\Phi_{ijkl}^{abcd}\rangle$$

4.229

Cluster operators
In the second quantization formalism:

$$\hat{T}_1 = \sum_{ia} t_i^a a_a^\dagger a_i, \quad \hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

- i, j: occupied orbitals
- a, b: virtual orbitals
- t_i^a,t_{ij}^{ab}: cluster amplitudes

4.230

Expression for the CC energy
Schrödinger equation:

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle$$

we transform as:

$$\hat{H}e^{\hat{T}}|\Phi_0\rangle = Ee^{\hat{T}}|\Phi_0\rangle$$
$$e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E|\Phi_0\rangle$$

Multiply from the left by $\langle\Phi_0|$ and excited functions:

$$E_{\text{CC}} = \langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle$$
$$0 = \langle\Phi_{ij\ldots}^{ab\cdots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle$$

Define the similarity transformed operator:

$$\bar{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$$

4.231

BCH expansion and why the exponential is not truncated
The Baker–Campbell–Hausdorff (BCH) expansion is a formula that rewrites a product of exponentials, or equivalently a similarity transformation, in terms of nested commutators. In coupled cluster theory, it allows us to express

$$\bar{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$$

without explicitly expanding the full exponential wavefunction.
For the similarity-transformed Hamiltonian, this gives:

$$\bar{H} = \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \frac{1}{24}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]$$

4.232

For the electronic Hamiltonian, which contains at most two-body operators, the nested commutator series terminates exactly after a finite number of terms. This happens because higher-order commutators cannot generate new connected contributions.
Importantly, the exponential itself is not truncated. In practice, one truncates the cluster operator, for example

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \quad (\text{CCSD}),$$

while the exponential remains formally complete:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \cdots$$

As a consequence, products such as $\hat{T}_2^2$ or $\hat{T}_1\hat{T}_2$ generate higher excitations implicitly, which is the key reason for the size-extensive character of coupled cluster theory.

4.233

CCD equations
For:

$$\Psi_{\text{CCD}} = e^{\hat{T}_2}|\Phi_0\rangle$$

Schrödinger equation:

$$\hat{H}e^{\hat{T}_2}|\Phi_0\rangle = E_{\text{CCD}}e^{\hat{T}_2}|\Phi_0\rangle$$

$$\langle\Phi_0|\hat{H} - E_{\text{CCD}}|e^{\hat{T}_2}\Phi_0\rangle = 0$$

Exponential expansion:

$$\langle\Phi_0|\hat{H} - E_{\text{CCD}}|(1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \cdots)\Phi_0\rangle = 0$$

Energy:

$$\begin{aligned} E_{\text{CCD}} &= \langle\Phi_0|\hat{H}|\Phi_0\rangle + \langle\Phi_0|\hat{H}\hat{T}_2|\Phi_0\rangle \\ &= E_{\text{HF}} + \sum_{\substack{i>j \\ a>b}} \langle\Phi_0|\hat{H}|\Phi_{ij}^{ab}\rangle t_{ij}^{ab} \\ &= E_{\text{HF}} + \sum_{\substack{i>j \\ a>b}} \langle ij||ab\rangle t_{ij}^{ab} \end{aligned}$$

4.234

CCD amplitude equations
Amplitude equation:

$$\langle\Phi_{ij}^{ab}|\hat{H} - E_{\text{CCD}}|e^{\hat{T}_2}\Phi_0\rangle = 0$$

can be expanded:

$$\langle\Phi_{ij}^{ab}|\hat{H}|\Phi_0\rangle + \langle\Phi_{ij}^{ab}|\hat{H} - E_{\text{CCD}}\hat{T}_2|\Phi_0\rangle + \langle\Phi_{ij}^{ab}|\hat{H} - E_{\text{CCD}}\frac{1}{2}\hat{T}_2^2|\Phi_0\rangle = 0$$

substituting components:

$$\langle \Phi_{ij}^{ab}|\hat{H}|\Phi_0\rangle + \langle \Phi_{ij}^{ab}|\hat{H} - E_{\mathrm{CCD}}|\Phi_{kl}^{cd}\rangle t_{kl}^{cd} + \frac{1}{2}\sum_{\substack{k>l>m>n \\ c>d>e>f}} \langle \Phi_{ij}^{ab}|\hat{H} - E_{\mathrm{CCD}}|\Phi_{klmn}^{cdef}\rangle t_{kl}^{cd} t_{mn}^{ef} = 0$$

Truncation schemes of the expansion:

$$\hat{T} = \hat{T}_2 \to \mathrm{CCD} \quad \hat{T} = \hat{T}_1 + \hat{T}_2 \to \mathrm{CCSD} \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \to \mathrm{CCSDT}$$

4.235

Iterative solution of CCD amplitudes

The CCD amplitude equations are obtained by projection:

$$\langle \Phi_{ij}^{ab}|\bar{H}|\Phi_0\rangle = 0,$$

which defines a nonlinear system for the amplitudes t_{ij}^{ab}.

Physically, these amplitudes measure the strength of double excitations $(i,j) \to (a,b)$. The solution is obtained iteratively by adjusting them until all projected components vanish, indicating that no further excitation can lower the energy.

In practice, one starts from the MP2 approximation:

$$t_{ij}^{ab,(0)} = \frac{\langle ab||ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = \frac{R_{ij}^{ab,(0)}}{D_{ij}^{ab,(0)}},$$

and then evaluates the residual

$$R_{ij}^{ab} = \langle \Phi_{ij}^{ab}|\bar{H}|\Phi_0\rangle.$$

The amplitudes are updated according to

$$t_{ij}^{ab} \leftarrow t_{ij}^{ab} + \frac{R_{ij}^{ab}}{D_{ij}^{ab}},$$

and the procedure is repeated until convergence $R_{ij}^{ab} \to 0$.

4.236

Example with one amplitude

A simple conceptual model illustrates the nonlinear character of CCD equations:

$$0 = v + Dt + Wt^2, \qquad t^{(n+1)} = -\frac{v + W(t^{(n)})^2}{D}$$

Here t represents a single double-excitation amplitude t_{ij}^{ab}, $v \equiv \langle ab||ij\rangle$ is the antisymmetrized two-electron integral (driving term),

$$D = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$$

is the orbital energy denominator, and Wt^2 schematically represents nonlinear coupling between amplitudes arising from higher-order terms in the similarity-transformed Hamiltonian.

The equation shows that amplitudes are determined as a fixed point of a nonlinear iteration.

4.237

Full CI vs. Full CC
Wavefunctions:

$$\Psi_{\text{CI}} = (1+\hat{C})|\Phi_0\rangle \qquad \Psi_{\text{CC}} = e^{\hat{T}}|\Phi_0\rangle$$

Operators:

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \hat{C}_4 + \cdots \qquad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$$

CC exponential expansion:

$$\begin{aligned} e^{\hat{T}} &= 1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_2^3 + \cdots \\ &= 1 + (\hat{T}_1 + \hat{T}_2 + \cdots) + \frac{1}{2}(\hat{T}_1 + \hat{T}_2 + \cdots)^2 + \cdots \\ &= 1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right) + \left(\hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3\right) + \cdots \end{aligned}$$

CI expansion:

$$|\Psi\rangle = |\Psi_0\rangle + \sum_S c_S|S\rangle + \sum_D c_D|D\rangle + \sum_T c_T|T\rangle + \sum_Q c_Q|Q\rangle + \cdots$$

4.238

Energy: CI vs. CC
CI is variational:

$$E \geq E_0^{\text{exact}}$$

CC is not:

$$E = \frac{\langle\Phi_0|e^{-T}\hat{H}e^{T}|\Phi_0\rangle}{\langle\Phi_0|\Phi_0\rangle}$$

For truncated T we obtain different left $\langle\Theta_B| = \langle\Phi_0|e^{-T}$ and right expansions $|\Theta_A\rangle = e^{T}|\Phi_0\rangle$ (not necessarily identical) $|\Theta_A\rangle \neq |\Theta_B\rangle$ and the expression for the energy:

$$E = \frac{\langle\Theta_B|\hat{H}|\Theta_A\rangle}{\langle\Phi_0|\Phi_0\rangle} = \frac{\sum_{ij} c_i^* d_j \langle\Psi_i|\hat{H}|\Psi_j\rangle}{\langle\Phi_0|\Phi_0\rangle} = \frac{\sum_i c_i^* d_i \varepsilon_i}{\langle\Phi_0|\Phi_0\rangle}$$

where the terms $c_i^* d_i$ can be negative.

4.239

Why truncated CC is size-extensive and CI is not
Size extensivity Energy scales linearly with the number of non-interacting, identical subsystems.

Truncated CI (e.g. CISD)

- CI uses a linear expansion: $|\Psi_{\text{CI}}\rangle = (1+\hat{C}_1+\hat{C}_2+\cdots)|\Phi_0\rangle$
- Truncation excludes higher excitations (e.g. triples, quadruples).
- Lack of disconnected excitations (e.g. double excitations from two separate monomers).
- **Does not reproduce the correct energy for uncoupled fragments.**

Truncated CC (e.g. CCSD)

- CC uses an exponential ansatz: $e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \cdots$
- Even with truncation, products of lower-order operators (e.g. $\hat{T}_1^2$) generate **disconnected excitations**. Disconnected contributions from $\hat{T}_1^2$, $\hat{T}_1\hat{T}_2$ etc. restore size extensivity.
- These excitations simulate higher-order excitations between fragments.
- **Ensures correct scaling: CCSD is size-extensive.**

4.240

4.10 Density Functional Theory

The wavefunction $\psi(x_1; x_2; \ldots; x_N)$ is a complicated eigenfunction of the Hamiltonian involving $4N$ variables and is not an observable. However, it is an amplitude of the probability density, which is a function of only 3 variables and, importantly, it can be determined experimentally!

The Hamiltonian depends on:	Ground state electron density:
number of electrons,	integrates to the **number of electrons**
positions of atomic nuclei,	has **cusps at the positions** of nuclei
charges of the nuclei	with **slope** determined by the nuclear charges

4.241

Electron Density
The wavefunction is the amplitude of the probability density.

$$\sum_{\sigma_1,\ldots,\sigma_N} \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \mathrm{d}^3\mathbf{r}_1 \cdots \mathrm{d}^3\mathbf{r}_N \, |\psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 = 1$$

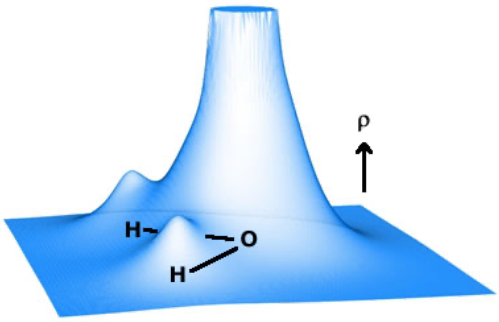
If we integrate the probability density over all spatial variables except one (any one), and over all spin variables, we obtain the *electron density* (an observable):

$$\rho(\mathbf{r}) = N \sum_{\sigma_1,\ldots,\sigma_N} \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \mathrm{d}^3\mathbf{r}_2 \cdots \mathrm{d}^3\mathbf{r}_N \, |\psi(\mathbf{r}, \sigma_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$$

4.242

contains complete information about the molecule:

- vanishes at infinity: $\lim_{r\to\infty} \rho(\mathbf{r}) = 0$
- integrates to the number of electrons: $\int_{\mathbb{R}^3} \rho(\mathbf{r}) \mathrm{d}^3\mathbf{r} = N$
- has a finite value at nuclear positions: $\rho(\mathbf{r} \to \mathbf{R}_\alpha)$
- and cusps near them, where the slope is directly related to nuclear charge: $\frac{\partial}{\partial r}\rho(\mathbf{r})|_{\mathbf{R}_\alpha} = -2Z_\alpha \rho(\mathbf{R}_\alpha)$



4.243

Density Matrix

This matrix generalizes the one-electron density:

$$\rho\left(\mathbf{r},\mathbf{r}'\right)=N\sum_{\sigma_1,\ldots,\sigma_N}\int_{\mathbb{R}^3}\cdots\int_{\mathbb{R}^3}\mathrm{d}^3\mathbf{r}_2\cdots\mathrm{d}^3\mathbf{r}_N\,\psi^*\left(\mathbf{r},\sigma_1,\mathbf{x}_2,\ldots,\mathbf{x}_N\right)\times \psi\left(\mathbf{r}',\sigma_1,\mathbf{x}_2,\ldots,\mathbf{x}_N\right)$$

It is necessary when determining expectation values of *non-multiplicative* operators from the density, for example:

$$\begin{aligned}\langle\psi|\hat{T}|\psi\rangle=&\sum_{\sigma_1,\ldots,\sigma_N}\int_{\mathbb{R}^3}\cdots\int_{\mathbb{R}^3}\mathrm{d}^3\mathbf{r}_1\cdots\mathrm{d}^3\mathbf{r}_N\,\psi^*\left(\mathbf{r}_1,\sigma_1,\mathbf{x}_2,\ldots,\mathbf{x}_N\right)\times\\&\left(-\frac{1}{2}\sum_{i=1}^{N}\nabla_{r_i}^2\right)\psi\left(\mathbf{r}_1',\sigma_1,\mathbf{x}_2,\ldots,\mathbf{x}_N\right)=\\=&-\frac{1}{2}\int_{\mathbb{R}^3}\mathrm{d}^3\mathbf{r}\left[\nabla_{r_i}^2\rho\left(\mathbf{r},\mathbf{r}'\right)\right]_{\mathbf{r}'=\mathbf{r}}\end{aligned}$$

The electron density is the diagonal of the density matrix: $\rho(\mathbf{r})=\rho(\mathbf{r},\mathbf{r})$, for example $\rho^{RHF}(\mathbf{r},\mathbf{r}')=2\sum_{i=1}^{N/2}\varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')$.

4.244

Pair Density

The probability density that if one electron is at $\mathbf{r}_1$, the second is at $\mathbf{r}_2$ simultaneously is a measure of *electron correlation*:

$$\gamma(\mathbf{r}_1,\mathbf{r}_2)=N(N-1)\sum_{\sigma_1,\ldots,\sigma_N}\int_{\mathbb{R}^3}\cdots\int_{\mathbb{R}^3}\mathrm{d}^3\mathbf{r}_3\cdots\mathrm{d}^3\mathbf{r}_N\times\left|\psi\left(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2,\mathbf{x}_3,\ldots,\mathbf{x}_N\right)\right|^2$$

It is normalized to the number of indistinguishable pairs, $N(N-1)$. Integrating over one coordinate gives the one-electron density:

$$\int_{\mathbb{R}^3}\mathrm{d}^3\mathbf{r}_2\,\gamma(\mathbf{r}_1,\mathbf{r}_2)=(N-1)\rho(\mathbf{r})$$

For example, in the Hartree-Fock method, only electrons with the same spin are correlated:

$$\gamma_{\alpha\alpha}^{RHF}(\mathbf{r}_1,\mathbf{r}_2)=\rho_\alpha(\mathbf{r}_1)\rho_\alpha(\mathbf{r}_2)-\rho_\alpha(\mathbf{r}_1,\mathbf{r}_2)\rho_\alpha(\mathbf{r}_2,\mathbf{r}_1)$$

$\gamma_{\alpha\alpha}$ vanishes as $\mathbf{r}_2 \to \mathbf{r}_1$, but:

$$\gamma_{\alpha\beta}^{RHF}(\mathbf{r}_1, \mathbf{r}_2) = \rho_\alpha(\mathbf{r}_1)\rho_\beta(\mathbf{r}_2).$$

4.245

First approximate expression for energy as a functional of electron density was proposed by Thomas and Fermi (1920).

Thomas-Fermi (TF) Model

- Kinetic energy functional $T_{TF}[\rho]$ for a uniform, non-interacting electron gas
- Electron repulsion is fully classical ($J[\rho]$)
- Dirac added the exchange energy term derived for a uniform non-interacting electron gas

$$E[\rho] = \underbrace{C_F \int_{\mathbb{R}^3} \rho^{5/3}(\mathbf{r}) \mathrm{d}^3\mathbf{r}}_{T_{TF}[\rho]} + V_{ne}[\rho] + J[\rho] \underbrace{- C_x \int_{\mathbb{R}^3} \rho^{4/3}(\mathbf{r}) \mathrm{d}^3\mathbf{r}}_{E_x[\rho]} + V_{nn}$$

Qualitatively correct results for atoms (for Ne–Xe, 96–100% of E_{HF}), but does not predict chemical bonding.

4.246

HF Energy as a Density Functional
In the Hartree-Fock method, the energy can be expressed as a functional of the density and density matrix:

$$\begin{aligned} E^{HF}[\rho] = & \underbrace{T[\rho]}_{\text{kinetic energy}} + \underbrace{V_{ne}[\rho]}_{\text{nucleus-electron attraction}} \\ & + \underbrace{J[\rho]}_{\text{classical electron repulsion}} - \underbrace{K[\rho]}_{\text{electron exchange}} \\ & + \underbrace{V_{nn}}_{\text{nuclear repulsion}} \end{aligned}$$

4.247

In the Hartree-Fock method, the energy can be expressed as a functional of the density and density matrix:

$$\begin{aligned} E^{HF}[\rho] = & -\frac{1}{2} \int_{\mathbb{R}^3} \mathrm{d}^3\mathbf{r} \left[\nabla_r^2 \rho\left(\mathbf{r}, \mathbf{r}'\right)\right]_{\mathbf{r}'=\mathbf{r}} + \int_{\mathbb{R}^3} v_{ne}(\mathbf{r}) \rho(\mathbf{r}) \mathrm{d}^3\mathbf{r} \\ & + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathrm{d}^3\mathbf{r}_1 \mathrm{d}^3\mathbf{r}_2 \frac{\gamma(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} + \sum_{\beta>\alpha}^{M} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \end{aligned}$$

where $E_{ee}[\gamma] = J[\rho] - E_{ncl}[\gamma]$ contains a *local* classical term:

$$\hat{j}\varphi(\mathbf{r}) = \left(\int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}^3\mathbf{r}' \right) \varphi(\mathbf{r})$$

and a *non-local* correlation term:

$$\hat{k}\varphi(r) = \frac{1}{2} \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi(\mathbf{r}') \mathrm{d}^3\mathbf{r}'$$

4.248

Hohenberg-Kohn Functional
Assuming the kinetic and electron-electron repulsion energies can be expressed as a functional of the electron density:

$$E[\rho] = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho] + V_{nn}$$

we group the energy functional into system-dependent and universal parts:

$$E[\rho] = V_{ext}[\rho] + F_{HK}[\rho]$$

where $F_{HK}[\rho]$ is the universal Hohenberg-Kohn functional valid for any system,

$$F_{HK}[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho]$$

and the system-dependent part:

$$V_{ext}[\rho] = \int_{\mathbb{R}^3} v_{ext}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}^3\mathbf{r}$$

4.249

$$E[\rho] = \int_{\mathbb{R}^3} v_{ext}(\mathbf{r})\rho(\mathbf{r})\mathrm{d}^3\mathbf{r} + \underbrace{T[\rho] + J[\rho] + E_{ncl}[\rho]}_{F_{HK}[\rho]}$$

First Hohenberg-Kohn Theorem (HK1)
The external potential $v_{ext}(\mathbf{r})$, and thus the total energy of the system, is a unique functional of the electron density $\rho(\mathbf{r})$. Therefore, there is a one-to-one mapping $v_{ext} \leftrightarrow \rho$.

Second Hohenberg-Kohn Theorem (HK2)
The density ρ_0 which minimizes the total energy is the exact ground state density. Thus, for any trial density (non-negative and integrating to N):

$$E[\rho] \geq E[\rho_0] = E_0$$

4.250

Hartree-Fock as an exact noninteracting particle model
The HF wavefunction can be seen as the exact wavefunction of a fictional system of non-interacting electrons:

- it ignores the electron correlation but correctly describes exchange
- electrons are treated as noninteracting fermions
- each electron is described by an orbital φ_i being a solution of the HF equation $\hat{f}\varphi_i = \varepsilon_i\varphi_i$

  $$\hat{f}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{ne}(\mathbf{r}) + v_{HF}(\mathbf{r})$$

  where $v_{\text{eff}} = v_{ne} + v_{HF}$ is the effective potential for electronic motion and

- the kinetic energy of electrons is:

$$T[\rho] = -\frac{1}{2}\int \nabla^2 \rho(\mathbf{r},\mathbf{r}')\big|_{\mathbf{r}'=\mathbf{r}} d^3r = -\sum_{i=1}^{N/2} \langle \varphi_i | \nabla^2 | \varphi_i \rangle \tag{4.251}$$

Noninteracting particles model
Let us define a system with Hamiltonian: $\hat{H}_S = \hat{T} + \hat{V}_S + \hat{V}_{nn}$ where

$$\hat{V}_S = \sum_{i=1}^{N} v_S(r_i)$$

There is no electron-electron interaction in $\hat{H}_S \Rightarrow$ a noninteracting system described by a single Slater determinant Ψ_S and the corresponding density ρ_S:

$$\Psi_S = |\varphi_1\alpha, \varphi_1\beta, \ldots, \varphi_{N/2}\alpha, \varphi_{N/2}\beta| \rightsquigarrow \rho_S$$

Each electron moves in an effective potential $v_{\text{eff}} = v_S$ thus, the orbitals (one-particle wavefunctions) can be obtained analogously as in the HF method $\hat{f}_{KS}\varphi_i = \varepsilon_i \varphi_i$ but with the so-called Kohn-Sham operator:

$$\hat{f}_{KS} = -\frac{1}{2}\nabla^2 + v_S(\mathbf{r}) \tag{4.252}$$

The Kohn-Sham Model
To obtain v_S we follow the Kohn and Sham recipe and want the non-interacting density

$$\rho_S(\mathbf{r}) = 2\sum_{i=1}^{N/2} |\varphi_i(\mathbf{r})|^2$$

to match the real system's density $\rho_S = \rho$. Since we do not know the explicit kinetic energy functional, it is approximated as in HF method as:

$$T_S[\rho] = -\sum_{i=1}^{N/2} \langle \varphi_i | \nabla^2 | \varphi_i \rangle$$

All other effects are absorbed into the *exchange-correlation* energy. (4.253)

Energy in the Kohn-Sham method
The total energy in the KS method reads:

$$\begin{aligned} E[\rho] =& T[\rho] + V_{ne}[\rho] + E_{ee}[\rho] + V_{nn} = \\ & T[\rho] + V_{ne}[\rho] + J[\rho] + E_{ncl}[\rho] + V_{nn} = \\ & T_S[\rho] + T[\rho] - T_S[\rho] + V_{ne}[\rho] + J[\rho] + E_{ncl}[\rho] + V_{nn} = \\ & T_S[\rho] + V_{ne}[\rho] + J[\rho] + \underbrace{T[\rho] - T_S[\rho] + E_{ncl}[\rho]}_{E_{xc}[\rho]} + V_{nn} = \end{aligned}$$

where $E_{xc}[\rho]$ is the exchange-correlation (xc) energy

$$E_{xc}[\rho] = T[\rho] - T_S[\rho] + E_{ncl}[\rho]$$

that accounts for exchange, correlation, self-interaction correction, and missing kinetic terms (not included in the noninteracting particle model). 4.254

Kohn-Sham Equations
Since total energy is a density functional

$$E[\rho] = T_S[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho] + V_{nn}$$

we may find its minimum using the variational method with the following constraint

$$\int \rho(\mathbf{r}) d^3 r = N$$

which leads to Kohn-Sham equations

$$\hat{f}_{KS}\varphi_i = \varepsilon_i \varphi_i$$

where

$$\hat{f}_{KS}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_S(\mathbf{r})$$

with an effective potential:

$$v_S(\mathbf{r}) = v_{ne}(\mathbf{r}) + J(\mathbf{r}) + v_{xc}(\mathbf{r})$$

However the explicit form of the exchange-correlation potential is not known:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

4.255

HF vs KS
Fock operator:

$$\hat{f}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{ne}(\mathbf{r}) + \hat{J}(\mathbf{r}) - \hat{K}(\mathbf{r})$$

Kohn-Sham operator:

$$\hat{f}_{KS}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{ne}(\mathbf{r}) + \hat{J}(\mathbf{r}) + v_{xc}(\mathbf{r})$$

HF	KS
nonlocal exchange operator	local operators only
parameter-free, well defined energy	energy depends on chosen functional
variational	variational only for exact functional
best energy in 1-electron approx.	exact xc functional would yield exact energy

4.256

KS-DFT Energy in an AO Basis
In practical calculations, molecular orbitals are expanded in an atomic-orbital (AO) basis:

$$\varphi_i(\mathbf{r}) = \sum_\mu C_{\mu i}\chi_\mu(\mathbf{r})$$

The KS energy is evaluated as:

$$E_{KS} = \underbrace{\sum_{\mu\nu} P_{\mu\nu}h_{\mu\nu}}_{\text{one-electron energy}} + \underbrace{\frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu}P_{\lambda\sigma}(\mu\nu|\lambda\sigma)}_{\text{Coulomb energy}} + E_{xc}[\rho] + E_{nn}$$

where

$$h_{\mu\nu} = \left\langle \chi_\mu \right| -\tfrac{1}{2}\nabla^2 + v_{ne} \left|\chi_\nu\right\rangle$$
$$(\mu\nu|\lambda\sigma) = \iint \chi_\mu(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)r_{12}^{-1}\chi_\lambda(\mathbf{r}_2)\chi_\sigma(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2.$$

Unlike HF exchange, E_{xc} is generally computed numerically on a real-space integration grid.

4.257

How Is the Energy Actually Computed?
PBE0 is an example of hybrid functional defined as

$$E_{xc}^{\text{PBE0}} = \frac{1}{4}E_x^{HF} + \frac{3}{4}E_x^{PBE} + E_c^{PBE}$$

The total energy becomes:

$$\begin{aligned} E^{PBE0} =& \sum_{\mu\nu} P_{\mu\nu}h_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu}P_{\lambda\sigma}(\mu\nu|\lambda\sigma) \\ &- \frac{1}{4}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu}P_{\lambda\sigma}(\mu\lambda|\nu\sigma) \\ &+ \frac{3}{4}E_x^{PBE}[\rho,\nabla\rho] + E_c^{PBE}[\rho,\nabla\rho] + E_{nn} \end{aligned}$$

Thus:

- Coulomb energy uses standard two-electron integrals.
- 25% of exact HF exchange is evaluated explicitly from exchange integrals.
- Remaining exchange and correlation are evaluated from density-dependent numerical quadrature.

4.258

What are E_x and E_c?
PBE belongs to the class of generalized gradient approximation (GGA) functionals and depends on both the density and its gradient:

$$E_{xc}^{PBE} = E_x^{PBE} + E_c^{PBE}$$

Exchange part

$$E_x^{PBE} = \int \rho(\mathbf{r})\, \varepsilon_x^{LDA}(\rho) F_x(s)\, d\mathbf{r}$$

where

$$\varepsilon_x^{LDA}(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}$$

is the uniform electron-gas exchange energy density and

$$F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}$$

is the enhancement factor depending on the reduced density gradient.

$$s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}}.$$

For PBE:

$$\kappa = 0.804, \qquad \mu = 0.21951.$$

4.259

The enhancement factor depends on the reduced density gradient:

$$F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}$$

which is a measure of density inhomogeneity:

$$s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}}$$

$\kappa = 0.804$ limits exchange enhancement and enforces exact constraints while $\mu = 0.21951$ controls the strength of gradient corrections.

4.260

PBE Correlation Energy

The PBE correlation functional modifies the local-density approximation (LDA) correlation:

$$E_c^{PBE} = \int \rho(\mathbf{r}) \left[\varepsilon_c^{LDA}(r_s, \zeta) + H(r_s, \zeta, t)\right] d\mathbf{r}$$

where

$$r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$$

is the Seitz radius and

$$\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta}$$

is the spin polarization.

The gradient correction H depends on the dimensionless gradient variable

$$t = \frac{|\nabla\rho|}{2k_s\phi\,\rho}$$

with screening wavevector k_s.

In practice:

$$E_c^{PBE} = \sum_g w_g \rho_g \left[\varepsilon_c^{LDA} + H \right]_g$$

is evaluated numerically on the integration grid. 4.261

How PBE Exchange-Correlation Is Evaluated
PBE is a GGA functional:

$$E_{xc}^{PBE} = \int f(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta)\, d\mathbf{r}$$

The electron density is reconstructed from the AO basis:

$$\rho(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r})$$

and similarly for density gradients

$$\nabla\rho(\mathbf{r}).$$

The integral is evaluated numerically on a grid:

$$E_{xc}^{PBE} \approx \sum_g w_g f(\rho_g, \nabla\rho_g)$$

where g labels grid points (Becke partitioning + radial/Lebedev grids).

$$\text{AO basis} \rightarrow \text{density matrix} \rightarrow \rho(\mathbf{r}_g) \rightarrow \text{XC quadrature}$$

4.262

Range-Separated Hybrid Functionals
A modern functional such as ωB97X-D combines short-range DFT exchange, long-range exact HF exchange, empirical correlation terms, and dispersion correction.
The exchange energy is partitioned:

$$\frac{1}{r_{12}} = \frac{1 - \mathrm{erf}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erf}(\omega r_{12})}{r_{12}}$$

leading schematically to:

$$E_x = c_x^{SR} E_x^{HF,SR} + c_x^{LR} E_x^{HF,LR} + E_x^{DFT}$$

The total energy becomes

$$E = E_{KS} + E_{disp}^D$$

where

$$E_{disp}^D = -\sum_{A>B} \frac{C_6^{AB}}{R_{AB}^6} f_{damp}(R_{AB}) + \cdots$$

accounts for London dispersion interactions. 4.263

What Does the Program Actually Compute?
For a functional such as PBE0 or ωB97X-D:

$$\begin{gathered}\text{AO basis} \rightarrow P_{\mu\nu} \\ \Downarrow \\ h_{\mu\nu},\ (\mu\nu|\lambda\sigma) \\ \Downarrow \\ \rho(\mathbf{r}_g),\ \nabla\rho(\mathbf{r}_g) \\ \Downarrow \\ E_J + E_x^{HF} + E_{xc}^{DFT} + E_{disp} \\ \Downarrow \\ E_{tot}\end{gathered}$$

The difference between functionals lies mainly in how E_{xc} is constructed and how much exact HF exchange is included.

4.264

4.11 Electronic Excitations in the RPA Paradigm

Electronic Excitations and the RPA Paradigm[4]
In the one-electron picture, a singly excited state can be described as the promotion of one electron from an occupied spin orbital k to a virtual spin orbital a:

$$|\Phi_{ak}\rangle = c_a^\dagger c_k |\Phi_0\rangle$$

where $|\Phi_0\rangle$ is the Hartree–Fock (HF) ground state.
The state $|\Phi_{ak}\rangle$ is an eigenstate of the zeroth-order HF Hamiltonian $\hat{H}_0$:

$$\begin{aligned}\hat{H}_0|\Phi_{ak}\rangle &= E_{ak}^{(0)}|\Phi_{ak}\rangle \\ \hat{H}_0 &= \sum_p \varepsilon_p\, c_p^\dagger c_p\end{aligned}$$

where ε_p are HF orbital energies and $E_{ak}^{(0)}$ denotes the zeroth-order contribution to the total energy of the excited state.
The full Hamiltonian can be partitioned into a zeroth-order contribution and a perturbation:

$$\hat{H} = \hat{H}_0 + \hat{H}_I$$

4.265

First-Order Corrections
The excitation energy is defined as:

$$\Delta E_{ak} = E_{ak} - E_0$$

[4] Schirmer, Phys. Chem. Chem. Phys., 2025, 27, 4992

where E_0 is the (exact) ground-state energy.
Using first-order perturbation theory, the excitation energy may be estimated as:

$$\Delta E^{(1)}_{ak} = \langle \Phi_{ak} | \hat{H} | \Phi_{ak} \rangle - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$$
$$\Delta E^{(1)}_{ak} = \varepsilon_a - \varepsilon_k - \upsilon_{akak} + \upsilon_{akka}$$

The zeroth-order contribution is given by the difference in HF orbital energies, where ε_a already includes Coulomb and exchange interactions with the unoccupied orbital k. This is corrected by the first-order contribution, where the Coulomb integral υ_{akak} accounts for electron–electron repulsion between the charge distributions of orbitals a and k, while the exchange integral υ_{akka} gives rise to singlet–triplet splitting of magnitude $2\upsilon_{akka}$.

4.266

Configuration Interaction and the Secular Matrix
The exact state $|\Psi_{ak}\rangle$ associated with $|\Phi_{ak}\rangle$ can be computed using the standard Configuration Interaction (CI) procedure:

$$|\Psi_n\rangle = \sum_J c_{Jn} |\Phi_J\rangle$$
$$|\Phi_J\rangle = \hat{C}_J |\Phi_0\rangle$$

where $\hat{C}_J$ are excitation operators:

$$\{\hat{C}_J\} = \left\{ 1;\ c_b^\dagger c_j;\ c_b^\dagger c_c^\dagger c_i c_j,\ b < c,\ i < j;\ \ldots \right\}$$

The representation of the shifted Hamiltonian $\hat{H} - E_0$ defines the CI secular matrix $\mathbb{H}$ with matrix elements:

$$H_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle - E_0 \delta_{IJ}$$

Solving the eigenvalue problem

$$\mathbb{H}\mathbb{C} = \mathbb{C}\Omega, \qquad \mathbb{C}^\dagger \mathbb{C} = \mathbb{I}$$

yields the eigenvector matrix $\mathbb{C}$ and a diagonal matrix of eigenvalues corresponding to excitation energies:

$$\Omega_n = E_n - E_0$$

4.267

Transition Moments
Transition moments are directly related to spectral intensities:

$$T_n = \langle \Psi_n | \hat{D} | \Psi_0 \rangle = \sum_J C^*_{Jn} \langle \Phi_J | \hat{D} | \Psi_0 \rangle$$

where $\hat{D}$ denotes an observable, for example a component of the dipole operator.

4.268

Block Structure of the CI Matrix

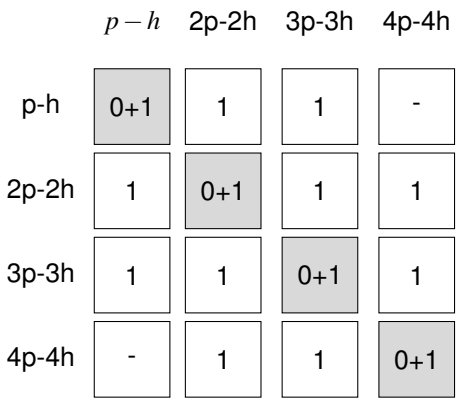


Figure 3: Block structure of the CI secular matrix $\mathbb{H}$ (neglecting coupling to the HF ground state). Indices 0 and 1 refer to matrix elements containing $\hat{H}_0$ and $\hat{H}_I$, respectively.

The coupling matrix elements H_{IJ} vanish whenever configurations I and J differ by more than two excitation classes. 4.269

Second-Order Energy Contributions

This implies that the second-order contribution to a singly excited-state energy contains admixtures of higher excitations:

$$\Delta E_{ak}^{(2)} = U_{ak}^{(2)}(ph) + U_{ak}^{(2)}(2p2h) + U_{ak}^{(2)}(3p3h) - E_0^{(2)}$$

These terms represent configuration mixing as well as relaxation and polarization effects. The first contribution may arise from improved occupied/virtual orbitals or partial admixture of states of different character.
The second term accounts for relaxation and polarization accompanying the excitation $a \leftarrow k$. The remaining electrons *relax* after removal of an electron from orbital k, while the electron promoted to a virtual orbital *polarizes* the charge distribution of the ionic core, leading to a substantial lowering of the first-order excitation energy. 4.270

Expansion of the Correlation Contribution

The third contribution accounts for electron correlation effects (which are typically stronger in the ground state than in excited states), leading to an increase in excitation energy:

$$\begin{aligned} U_{ak}^{(2)}(3p3h) - E_0^{(2)} = &\sum_{b,ij} \frac{|v_{ab[ij]}|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \\ &+ \sum_{j,bc} \frac{|v_{bc[kj]}|^2}{\varepsilon_b + \varepsilon_c - \varepsilon_k - \varepsilon_j} \\ &- \sum_{j,b} \frac{|v_{ab[kj]}|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_k - \varepsilon_j} \end{aligned}$$

where $v_{ab[ij]}$ denotes antisymmetrized Coulomb integrals $\langle ab||ij\rangle$. 4.271

Time-Dependent Hartree–Fock

The Random Phase Approximation (RPA) provides excitation energies within the linear-response formalism. It can be derived from the time-dependent Hartree–Fock (TDHF) equations in the limit of small perturbations.

The TDHF equation reads:

$$i\frac{d}{dt}|\phi_k(t)\rangle = \hat{H}_0(t)|\phi_k(t)\rangle$$

where $\hat{H}_0(t)$ is the time-dependent Fock operator.

Assuming that HF spin orbitals are perturbed by a weak external time-dependent field leads to small deviations from the ground state:

$$|\phi_k(t)\rangle = |\phi_k^{(0)}\rangle + |\delta\phi_k(t)\rangle$$

To express the fluctuation in a complete basis, it is expanded in terms of virtual (unoccupied) orbitals. The fluctuation may be decomposed into particle–hole ($p-h$) excitations:

$$|\delta\phi_k(t)\rangle = \sum_a \left(x_{ak}e^{-i\omega t} + y_{ak}^* e^{i\omega t}\right)|\phi_a^{(0)}\rangle$$

4.272

RPA as a Pseudo-Eigenvalue Problem

Substituting the expansion into the linearized TDHF equation (retaining only first-order terms in the perturbation) yields a coupled system of equations for the *excitation amplitudes* $\boldsymbol{x}$ and *relaxation amplitudes* $\boldsymbol{y}$, taking the form of an RPA pseudo-eigenvalue problem:

$$\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ -\mathbb{B}^* & -\mathbb{A}^* \end{pmatrix}\begin{pmatrix} \boldsymbol{x}_m \\ \boldsymbol{y}_m \end{pmatrix} = \omega_m \begin{pmatrix} \boldsymbol{x}_m \\ -\boldsymbol{y}_m \end{pmatrix}$$

where $\mathbb{A}$ and $\mathbb{B}$ are blocks of the Hermitian matrix $\mathbb{M}$, defined in the configuration space of particle–hole ($p-h$) excitations and hole–particle ($h-p$) relaxation modes.

The matrix elements are given by:

$$A_{ak,bl} = (\varepsilon_a - \varepsilon_k)\delta_{ab}\delta_{kl} - \upsilon_{albk} + \upsilon_{alkb}$$
$$B_{ak,lb} = -\upsilon_{ablk} + \upsilon_{abkl}$$

The matrix $\mathbb{A}$ resembles the CIS secular matrix, whereas $\mathbb{B}$ accounts for coupling between $p-h$ and $h-p$ configurations.

4.273

A Simple 2×2 RPA Example

2×2 RPA Example

For illustration, consider a simplified 2×2 RPA matrix, where a and b are real numbers:

$$\begin{pmatrix} a & b \\ b & a \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \omega \begin{pmatrix} x \\ -y \end{pmatrix}$$

The two eigenvalue solutions are:

$$\omega_{\pm} = \pm\sqrt{a^2 - b^2} = \pm|a|\sqrt{1 - \tfrac{b^2}{a^2}}$$

Thus, if $|b| > |a|$, complex eigenvalues emerge. Otherwise, the square root may be expanded as a power series in $\frac{b^2}{a^2}$:

$$\omega_{+} = a - \tfrac{b^2}{2a} + \cdots$$

4.274

RPA Transition Moments

Transition moments in the RPA formalism are expressed as:

$$T_m = \sum_{a,k} \left(x^*_{ak,m} d_{ak} + y^*_{ka,m} d_{ka} \right)$$

where d_{pq} are matrix elements of the transition operator. 4.275

Perturbative Expansion of the RPA Excitation Energy

The excitation energy obtained within the RPA approximation may be expanded perturbatively as:

$$\Delta E^{\mathrm{RPA}}_{ak} = \varepsilon_a - \varepsilon_k - \upsilon_{akak} + \upsilon_{akka} + U^{(2)}_{ak}(\mathrm{ph}) + U^{(2)}_{ak}(\mathrm{hp}) + \mathscr{O}(3)$$

This expression shows that the RPA excitation energy is correct through first order (the same applies to transition moments), whereas at second order only $p-h$ and $h-p$ contributions are included.

Relaxation and polarization effects contained in the missing $U^{(2)}_{ak}(2p2h)$ contribution are neglected.

The $h-p$ terms arise from the unusual coupling of the excitation $a \leftarrow k$ to hole–particle relaxation configurations.

The relaxation (hole–particle) contribution:

$$U^{(2)}_{ak}(\mathrm{hp}) = -\sum_{b,j} \frac{|\upsilon_{ab[kj]}|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_k - \varepsilon_j}$$

has the same mathematical form as the negative term in the $3p$–$3h$ contribution. Although it lowers the excitation energy, its physical interpretation remains questionable. 4.276

Time-Dependent DFT in Linear Response

- In linear-response time-dependent DFT (LR-TDDFT), excitation energies are computed within the linear regime.
- The formalism is analogous to RPA, but based on Kohn–Sham (KS) orbitals and orbital energies.
- It is derived from the time-dependent Kohn–Sham equations within the adiabatic approximation.

4.277

RPA-Type Equation in LR-TDDFT

The LR-TDDFT eigenvalue problem has the same structure as RPA:

$$\begin{pmatrix} \tilde{\mathbb{A}} & \tilde{\mathbb{B}} \\ -\tilde{\mathbb{B}}^* & -\tilde{\mathbb{A}}^* \end{pmatrix} \begin{pmatrix} \boldsymbol{x}_m \\ \boldsymbol{y}_m \end{pmatrix} = \omega_m \begin{pmatrix} \boldsymbol{x}_m \\ -\boldsymbol{y}_m \end{pmatrix}$$

- Kohn–Sham orbital energies ε_a^{KS} are used instead of HF orbital energies.
- Matrix elements are modified through the exchange–correlation kernel f_{xc}.

4.278

Matrix Elements in LR-TDDFT

The matrices $\tilde{\mathbb{A}}$ and $\tilde{\mathbb{B}}$ are defined as:

$$\tilde{A}_{ak,bl} = \varepsilon_a^{KS} - \varepsilon_k^{KS} + f_{alkb}^{\text{xc}} + \upsilon_{alkb}$$
$$\tilde{B}_{ak,lb} = f_{abkl}^{\text{xc}} + \upsilon_{abkl}$$

Here, the Coulomb integrals appearing in $\mathbb{A}$ are replaced by matrix elements of the exchange–correlation kernel:

$$f_{alkb}^{\text{xc}} = \langle \phi_a \phi_l | f_{\text{xc}}[n_0] | \phi_k \phi_b \rangle$$

where

$$f_{\text{xc}}[n](\mathbf{r}, \mathbf{r}') = \frac{\delta v_{\text{xc}}[n](\mathbf{r})}{\delta n(\mathbf{r}')}$$

The LR-TDDFT equations rely on the so-called adiabatic approximation, in which xc functionals depend on time only through the time-dependent electron density $n(t)$. This makes it possible to employ ground-state exchange–correlation functionals $E_{\text{xc}}[n]$.

4.279

Comparison with RPA

- LR-TDDFT improves upon RPA by using KS solutions and approximate correlation effects through f_{xc}.
- It remains restricted to single excitations and does not include relaxation/polarization effects, unless specialized kernels are introduced.
- First-order contributions are approximate, whereas second-order correlation effects are only partially included.

The perturbative expansion of the excitation energy reveals the absence of the Coulomb repulsion term $-v_{akak}$, which describes electron repulsion between orbitals a and k:

$$\Delta E_{ak}^{\mathsf{TDDFT}} = \varepsilon_a^{KS} - \varepsilon_k^{KS} + f_{akka}^{\mathsf{xc}} + v_{akka} + \tilde{U}_{ak}^{(2)}(\mathsf{ph}) + \tilde{U}_{ak}^{(2)}(\mathsf{hp}) + \mathscr{O}(3)$$

The quantity f_{akka}^{xc} does not provide an adequate replacement. At least for local functionals, the approximate $1/R$ dependence of the original Coulomb interaction between localized orbitals a and k cannot be recovered.

As a consequence, Rydberg excitations and charge-transfer (CT) excitations are described poorly.

4.280

Range Separation (ω)

One way to mitigate such deficiencies is to employ functionals containing 100% Hartree–Fock exchange (e.g. M06-HF), although these typically involve many empirically fitted parameters.

An alternative is to retain the form of popular GGA or hybrid functionals at short range, while introducing 100% HF exchange for long-range interactions.

These are the so-called range-separated hybrid (RSH) functionals, in which the Coulomb interaction is partitioned using the error function:

$$\frac{1}{r_{12}} = \underbrace{\frac{1-\mathrm{erf}(\omega r_{12})}{r_{12}}}_{\text{short range}} + \underbrace{\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}}_{\text{long range}}$$

- ω is the range-separation parameter (in Bohr^{-1}).
- It controls how rapidly long-range exchange is switched on.
- Used, for example, in CAM-B3LYP, ωB97X, and LC-BLYP.

4.281

Performance of TDDFT

Fraction of short-range c_{HF}^{sr} and long-range c_{HF}^{lr} Hartree–Fock exchange in selected DFT functionals.

Functional	c_{HF}^{sr}	c_{HF}^{lr}	ω
CIS/RPA	1.00	1.00	–
B3LYP	0.20	–	–
BHLYP	0.50	–	–
CAM-B3LYP	0.19	0.65	0.33
CAMh-B3LYP	0.19	0.50	0.33
BP86	0.00	–	–
PBE	0.00	–	–
PBE0	0.25	–	–
PBE50	0.50	–	–
ωPBE	0.00	1.00	0.30
ωhPBE0	0.25	0.50	0.20
ωPBEh	0.20	1.00	0.20
ωB97X	0.16	1.00	0.30
ωB97X-D	0.22	1.00	0.20
BNL	0.00	1.00	–
M06-2X	0.54	–	–
M11	0.43	1.00	–
M11-L	0.00	–	–

4.282

4.283

4.284

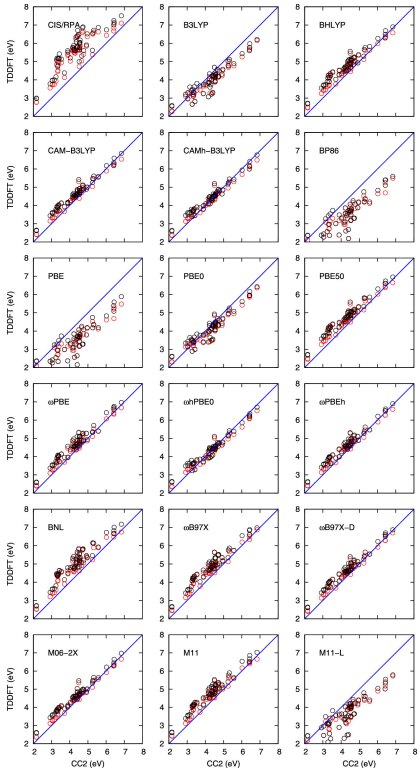


Figure 4: Performance of TDDFT functionals compared with CC2 excitation energies computed using the def2-TZVP basis set. Vertical excitation energies (VEEs, in eV) calculated with TDDFT and TDA are shown in red and black, respectively [J. Chem. Theory Comput. 2020, 16, 1, 587].

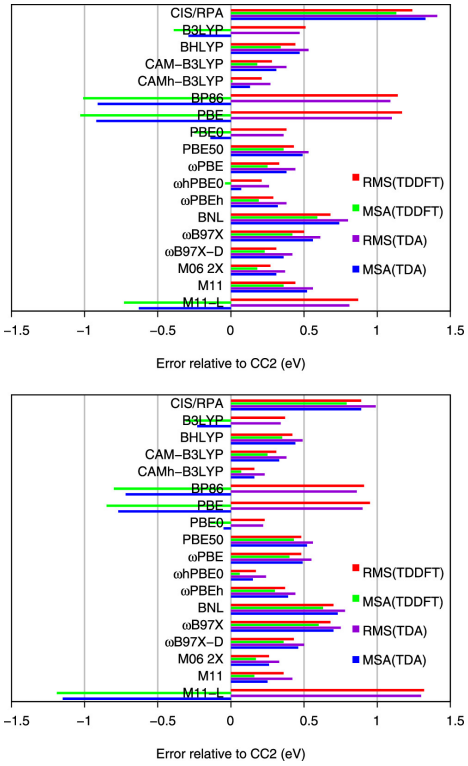


Figure 5: RMS and MSA deviations (in eV) between excitation energies computed using TDDFT, TDA, and CC2 with the def2-TZVP basis set (upper panel) and aug-def2-TZVP(lower panel). The five lowest excited states of selected organic chromophores were included in the comparison.

Chapter 5
Computational Chemistry

5.285

5.1 Chemical Accuracy

Required Accuracy for Realistic Chemical Predictions

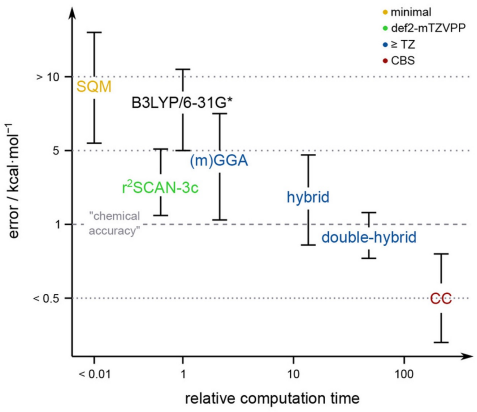
- **Chemical accuracy:** 1 kcal/mol
  - 4.184 kJ/mol
  - 4.33×10^{-2} eV
  - 350 cm^{-1}
  - 1.59 mHartree
- **Sub-chemical accuracy:** 1 kJ/mol or better

5.2 Good Practices in KS-DFT

Limitations of DFT
Density Functional Theory (DFT) is generally not sufficiently accurate to achieve chemical accuracy on its own.

5.286

Accuracy and computational cost in typical thermochemical applications of popular quantum chemistry methods:[5]



5.287

Best Practices in Computational Chemistry – DFT [6]
Accuracy and computational cost:

[5] **SQM** = semiempirical quantum chemistry method; **CBS** = complete basis set limit.
[6] Based on Grimme et al., Angew. Chem. Int. Ed., 61, 2022

- Wavefunction-based methods, such as coupled-cluster (CC) approaches (e.g. CCSD(T)), provide reference-quality results with an accuracy better than 1 kcal/mol **for typical chemical energy changes in nearly any well-behaved single-reference system.**
- Lower levels of the DFT hierarchy, ranging from composite methods with small basis sets (e.g. r2SCAN-3c), through (m)GGA functionals to hybrid functionals, provide systematically improved results when used together with sufficiently large basis sets.
- The most advanced double-hybrid functionals often yield results approaching reference-level coupled-cluster quality.

5.288

Meaning of the "3c" Acronym in Composite Methods

What Does the "3c" Suffix Mean in Methods Such as r2SCAN-3c?

- **3c = three empirical corrections that compensate for the use of small basis sets:**
  1. **D3** – Dispersion correction (e.g. Grimme's D3(BJ))
     Accounts for dispersion interactions that are missing in standard DFT.
  2. **gCP** – Geometrical Counterpoise Correction
     Corrects basis-set superposition error (BSSE).
  3. **SRB** – Short-range basis-set incompleteness correction
     Improves the description of short-range interactions.

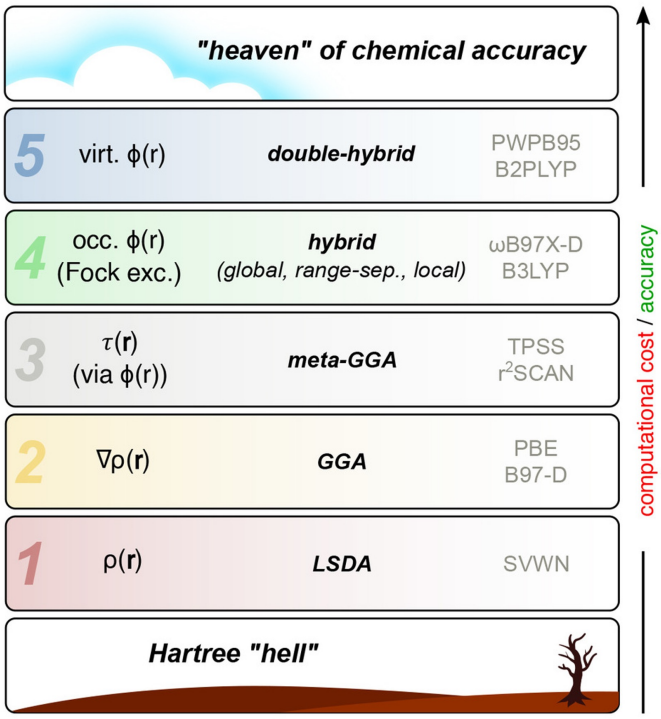
Applications of "3c" Methods

- Rapid energy estimates.
- Studies of large molecules and materials.
- Geometry and conformational analysis.

5.289

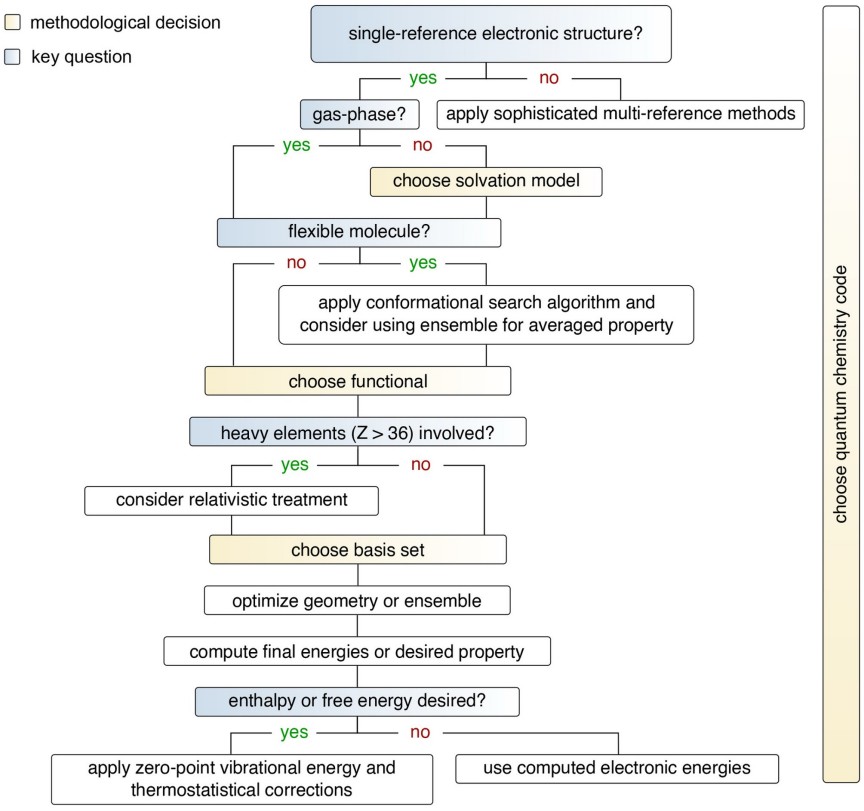
Perdew's Jacob's Ladder of DFT

Classification of density functionals according to Perdew's "Jacob's Ladder": [7]



5.290

Decision Workflow for Selecting a Computational Method



5.291

[7] ρ = electron density, τ = kinetic energy density, φ = molecular orbital, Fock exc. = Fock exchange (exact exchange from wavefunction theory).

Electronic Structure and Solvation Effects

Electronic Structure

- Check for multireference character using simple indicators (e.g. HOMO–LUMO gap, spin contamination).
- Exercise particular caution for open-shell systems (especially low-spin cases).
- Avoid single-reference methods, such as DFT, for genuinely multireference systems.

Solvation Effects

- Choose a model or phase that is as close as possible to the experimental conditions.
- Use continuum solvation models for molecules in solution; physically complete approaches, such as COSMO-RS or SMD (PCM), are generally preferred.
- Be cautious for charged systems, where continuum models may become inaccurate (the higher the charge density, the larger the potential error).
- Consider explicit solvation when necessary.

5.292

Molecular Structure and Conformer Searching

Molecular Structure

- Assess the influence of structural flexibility and conformational effects through conformational-space exploration.
- Use automated conformer-search algorithms, for example CREST or GOAT.
- Attempt to identify and verify the lowest-energy conformer.
- Consider Boltzmann-weighted averaging when appropriate.

5.293

Choosing a Functional

- Choose the functional carefully, guided by the chemical system and the computational objective, rather than popularity.
- Always include a dispersion correction.
- Consider reliable cost–accuracy tradeoffs and evaluate (m)GGA functionals. Hybrid functionals are generally more accurate, but substantially more computationally demanding.
- Check consistency of results across different functional classes (e.g. comparing hybrid and (m)GGA functionals).
- For critical applications, test hybrid functionals with different fractions of Hartree–Fock exchange.
- Consider validated multilevel approaches and composite methods for larger systems.

5.294

Comparison of DFT Functionals[8]

Root-mean-square deviations (RMSD, kcal/mol) for the 20 density functionals with the lowest RMSD among 200 assessed functionals. NCED – easy noncovalent dimers, NCEC – easy noncovalent clusters, NCD – difficult noncovalent dimers, IE – easy isomerization energies, ID – difficult isomerization energies, TCE – easy thermochemistry, TCD – difficult thermochemistry, BH – barrier heights.

Functional	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH	EBL	EBE
SPW92	2.14	37.77	7.60	2.22	6.76	42.23	65.35	19.55	0.195	2.81
PBE	1.96	4.08	3.26	1.15	6.53	9.22	15.58	9.17	0.327	2.16
TPSS	2.58	8.90	2.63	1.39	8.44	5.94	10.45	8.03	0.398	2.80
B3LYP	2.86	8.91	1.77	1.49	11.10	5.24	11.97	5.96	0.643	3.04
PBE-D3(BJ)	0.46	5.78	3.67	0.71	5.19	9.67	17.20	9.99	0.049	0.42
revPBE-D3(BJ)	0.49	6.60	2.54	0.77	5.21	6.60	9.91	8.30	0.053	0.44
BLYP-D3(BJ)	0.34	2.18	2.82	0.68	11.40	6.63	11.11	9.91	0.031	0.25
B97-D3(BJ)	0.47	4.82	2.52	0.78	9.15	4.66	7.92	8.32	0.045	0.42
TPSS-D3(BJ)	0.38	2.28	3.06	0.69	6.47	5.88	8.86	8.72	0.070	0.33
SCAN-D3(BJ)	0.54	9.18	3.41	0.55	4.46	5.25	6.39	7.83	0.037	0.60
M06-L	0.55	2.20	1.87	0.71	10.16	5.44	12.97	6.85	0.043	0.60
B97M-rV	0.22	0.67	2.04	0.28	6.45	3.57	4.78	4.36	0.025	0.17
PBE0-D3(BJ)	0.44	4.45	2.28	0.58	3.47	4.76	8.72	4.91	0.043	0.46
B3LYP-D3(BJ)	0.31	3.02	1.88	0.49	8.51	3.72	5.97	5.65	0.022	0.37
ωB97X-D	0.37	1.01	1.46	0.67	3.11	3.44	5.79	2.34	0.038	0.42
ωB97X-V	0.24	0.64	1.23	0.27	2.72	3.41	5.01	2.44	0.042	0.15
TPSSh-D3(BJ)	0.36	1.73	2.49	0.62	5.29	5.55	5.92	6.63	0.068	0.33
M06-2X	0.43	2.52	0.99	0.50	5.56	3.29	7.23	2.57	0.077	0.33
MN15	0.47	1.83	0.96	0.71	4.06	3.76	6.44	1.98	0.042	0.60
ωB97M-V	0.18	0.48	1.13	0.28	2.05	2.48	4.30	1.68	0.014	0.15
Minimum	**0.18**	**0.48**	**0.91**	**0.27**	**2.05**	**2.48**	**4.30**	**1.68**	**0.014**	**0.15**
Best	ωB97M-V	ωB97M-V	M08-SO	B97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97X-V

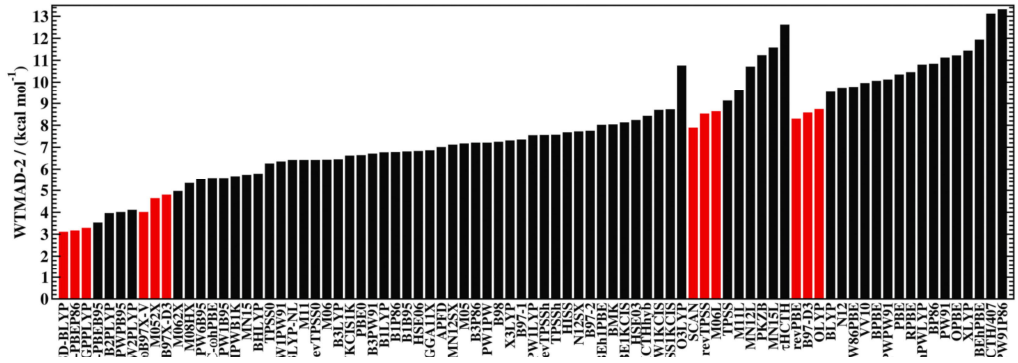
5.295

[8] Mardirossian and Head-Gordon, Mol. Phys. 2017, 115 (19), 2315–2372. https://doi.org/10.1080/00268976.2017.1333644

Comparison of DFT Functionals [9]

WTMAD values (weighted total mean absolute deviation) for the GMTKN55 benchmark set for 83 dispersion-corrected functionals (in kcal/mol).
Red bars denote the three best-performing methods within each rung of Jacob's ladder.
The D3 suffix has been omitted unless required to avoid ambiguity.

GMTKN55 benchmark



5.296

Choice of Basis Set in DFT Calculations

Basis Set Selection

- The most commonly used Gaussian basis sets include: Pople (e.g. 6-31G), Dunning (cc-pVXZ), Jensen (pc(seg)-X), and *Ahlrichs (def2-XVP)*.
- Pople basis sets (6-31G*, 6-311G**) and Dunning basis sets (cc-pVXZ) are generally not recommended for routine DFT calculations.
- Ahlrichs basis sets (def2-XVP) are more efficient and widely available across a larger portion of the periodic table.

5.297

[9] Goerigk et al., PCCP 2017, 19 (48), 32184–32215. https://doi.org/10.1039/C7CP04913G

Basis Set Selection

- Pay attention to basis-set incompleteness error (BSIE) and basis-set superposition error (BSSE).
- Use at least $\geq$TZ-quality basis sets for energetic properties.
- Consider adding polarization functions (e.g. def2-XVPP, 6-311G(2df,2p)) to increase flexibility.
- Include diffuse functions for anions, dipole moments, and polarizability calculations (e.g. **ma**-XVP, def2-XVP**D**, 6-31**+**G).
- Check basis-set convergence by increasing or decreasing the cardinal number by one.
- For heavy elements ($Z > 36$), use effective core potentials (def2-ECP), or alternatively X2C, ZORA, or DKH with dedicated basis sets (e.g. cc-pVDZ-DK).
- For post-HF calculations, avoid basis sets smaller than VDZ (for qualitative analysis) or VTZ (for semi-quantitative work).

  Dunning basis sets (cc-pVXZ) are usually the preferred choice.

5.298

Comparison with Experiment

- Computational models usually correspond to *0 K and 0 Pa*!
- Zero-point vibrational energy (ZPVE) and thermochemical corrections should be included.
- Be aware of concentration-induced free-energy shifts (a correction $\Delta G = RT \ln V_m \approx 1.89$ kcal/mol must be added to the enthalpy).
- For large systems with low vibrational frequencies (< 50–100 cm^{-1}), the mRRHO model (available, for example, in GoodVibes) is often recommended.

5.299

Decision Matrix: Methods and Basis Sets

- The matrix summarizes recommendations for different computational tasks.
- Color coding:

  red – not recommended,

  yellow – caution,

  green – appropriate,

  blue – optimal balance between cost and accuracy.
- Typical issues considered include self-interaction error (SIE), BSSE, BSIE, and excessive computational cost.

functional class / recommendation	basis size	structures	frequencies	conformers	reaction energies	barriers	NCI
(meta-)GGA	DZ		structure[b]	BSIE	SIE, BSIE	SIE, BSIE	SIE, BSIE
	TZ				SIE, BSSE	SIE, BSSE	SIE, BSSE
B97M-V, r^{2}SCAN [a], TPSS	QZ	excessive	excessive		SIE	SIE	SIE
hybrid	DZ		structure[b]	BSIE	BSIE	BSIE, SIE[c]	BSIE
	TZ				BSSE	BSSE, SIE[c]	BSSE
PW6B95, PBE0	QZ	excessive	excessive			SIE[c]	
range-separated hybrid	DZ		structure[b]	BSIE	BSIE	BSIE	BSIE
	TZ				BSSE	BSSE	BSSE
ωB97X-V, ωB97X-D4, ωB97M-V, ωB97M-D4,	QZ	excessive	excessive				
double-hybrid	DZ		structure[b], excessive	BSIE	BSIE	BSIE	BSIE
	TZ	excessive	excessive	BSSE	BSSE	BSSE	BSSE
PWPB95, ωB97M(2), revDSD-PBEP86-D4	QZ	excessive	excessive				
composite methods							
B97-3c	TZ				SIE	SIE	SIE
r^{2}SCAN-3c [a]	TZ				SIE	SIE	SIE
PBEh-3c [d]	DZ				BSIE	BSIE	BSIE
commonly used combinations							
B3LYP/6-31G*	DZ	BSSE, no-D	structure[b], no-D	BSSE, no-D	BSSE, no-D	BSSE, no-D	BSSE, no-D
BP86-D3	TZ				SIE, BSSE	SIE, BSSE	SIE, BSSE
M06-2X/6-311G** [a,d,e]	TZ						

[a] High dependency on the size of the numerical integration grid.

[b] If the structure is reasonable (DZ ≈ TZ), GGA/DZ or even semi-empirical frequencies are sufficient. If not, use SPH.

[c] Self-interaction error can limit the accuracy for hybrid functionals with small amounts of Fock exchange (< 25%).

[d] The large amount of Fock exchange can cause pronounced errors for transition metal complexes.

[e] 6-311G** behaves like a double-zeta basis set and should be used with caution.

not recommended — intermediate — accurate — recommended / good cost-benefit-ratio

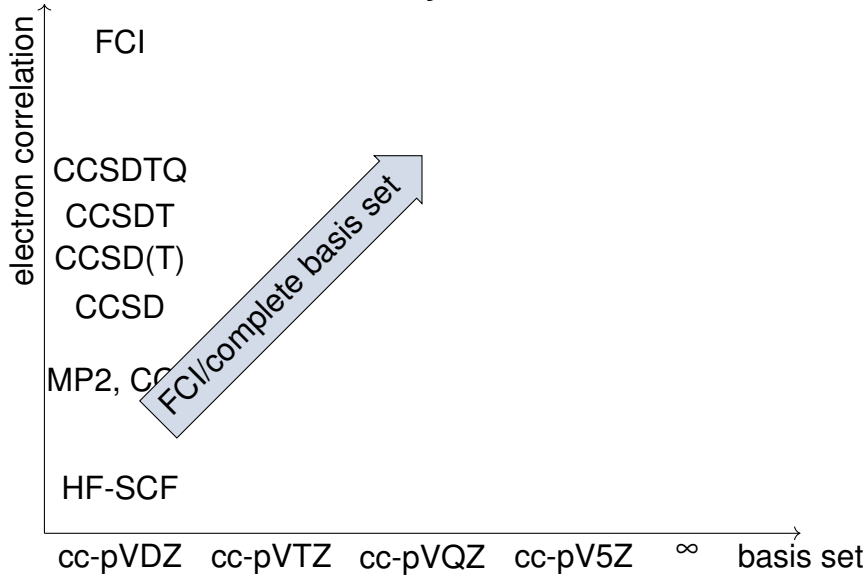
Quantum Chemistry Software Packages

- **GAUSSIAN** – popular, user-friendly, supports ONIOM.
- **GAMESS(US)** – multiconfigurational methods (ORMAS, MCQDPT), EFP, and EDA analysis.
- **TURBOMOLE** – fast, advanced DFT algorithms, ADC(2), CC2.
- **ORCA** – efficient DFT and wavefunction methods (NEVPT2), fast implementation of hybrid functionals (RIJCOSX), rich selection of tools for molecular spectroscopy.
- **Q-Chem** – broad selection of functionals (ωB97X-V), EDA analysis, TDDFT, and methods for noncovalent interactions (SAPT, DFT-C).
- **Psi4** – modular, easy scripting and integration, SAPT.
- **Molpro** – advanced RPA methods, ACFDT, WFT-in-DFT embedding, SAPT.
- **OpenMolcas** – multiconfigurational methods: XMS-CASPT2, RASSCF, RASSI.
- **BAGEL** – multiconfigurational methods: XMS-CASPT2, MCQDPT.

5.302

5.3 Good Practices in WFT

Approximate Quantum Chemistry Methods [10]



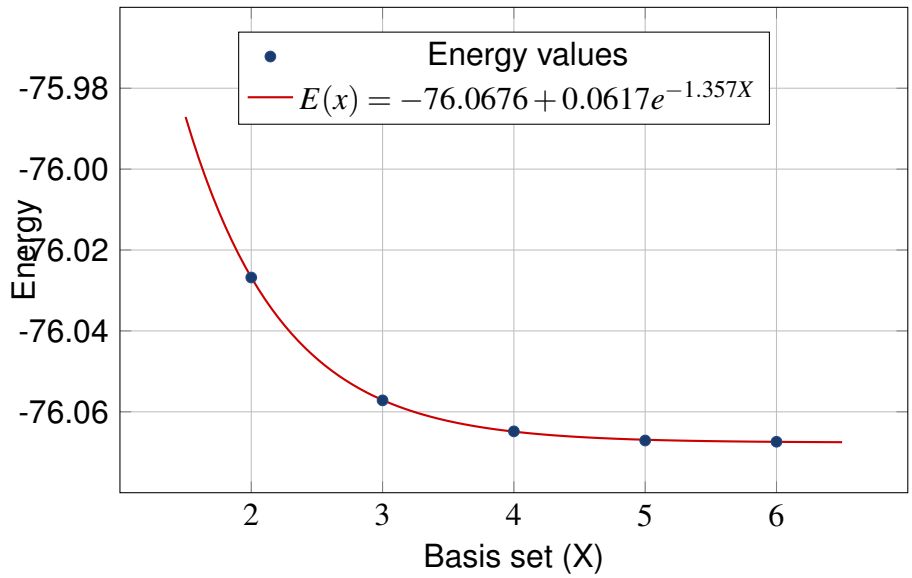
5.303

HF Limit [11]

[10] Based on lectures by Jürgen Gauss (ESQC)
[11] D. Feller, J. Chem. Phys. 98, 7059 (1993)

Extrapolation to the Complete Basis Set Limit

$$E(\text{HF-SCF/cc-pVXZ}) = E_\infty(\text{HF-SCF}) + a\exp(-bX)$$

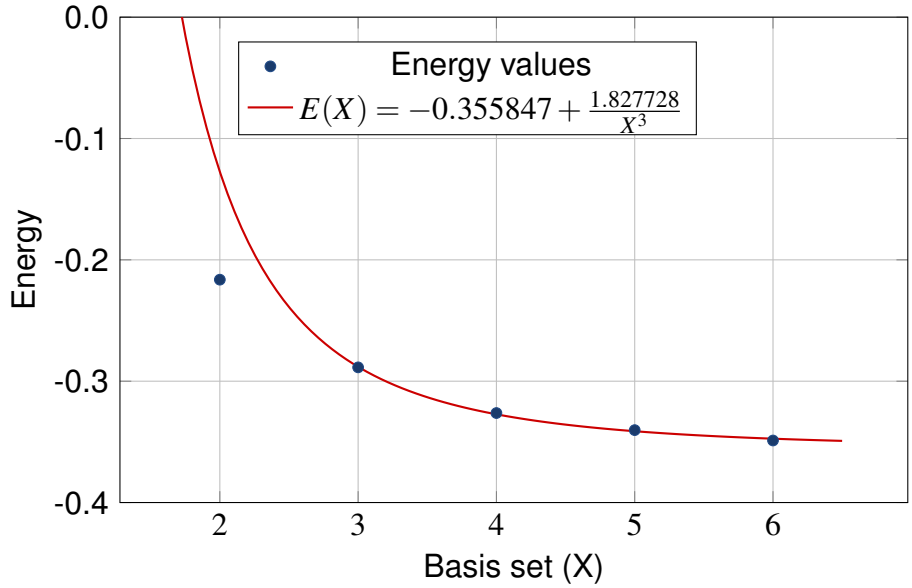


5.304

Convergence of the Correlation Energy [12]

Correlation Energy Extrapolation

$$\Delta E_\infty(\text{CC}) = \Delta E(\text{CC/aug-cc-pVXZ}) - \frac{c}{X^3}$$



5.305

[12] Helgaker et al., J. Chem. Phys. 106, 9639 (1997)

Magnitude of the Correlation Energy

- The correlation energy typically accounts for less than 1% of the total energy.

	H_2O	HCN
E^{HF}	-76.068	-92.916
ΔE_{corr}	-0.372	-0.518
ΔE_{rel}	-0.052	-0.044

5.306

Importance of Electron Correlation

- Correlation energy depends primarily on valence electrons.
- 0.001 Hartree corresponds to 2.6255 kJ/mol.
- Correlation effects are always important for bond breaking and bond formation.

5.307

Example: CO Dissociation (Atomic Units)

$$\mathrm{CO} \rightarrow \mathrm{C}(^3\mathrm{P}) + \mathrm{O}(^3\mathrm{P})$$

	C	O	CO	D_e (a.u.)
E_{HF}	-37.693774	-74.819232	-112.790997	0.277991
E_{corr}	-0.151537	-0.248978	-0.536591	0.136076
E_{total}	-37.845307	-75.068210	-113.327588	0.414071

5.308

Example: CO Dissociation (kJ/mol)

$$\mathrm{CO} \rightarrow \mathrm{C}(^3\mathrm{P}) + \mathrm{O}(^3\mathrm{P})$$

	C	O	CO	D_e (kJ/mol)
E_{HF}	-37.693774	-74.819232	-112.790997	729.9
E_{corr}	-0.151537	-0.248978	-0.536591	357.3
E_{total}	-37.845307	-75.068210	-113.327588	1087.2

Electron correlation effects are substantial.

5.309

Importance of Double Excitations

- MP2 typically recovers more than 95% of the correlation energy.
- Møller–Plesset perturbation theory (MPPT) converges monotonically within either even or odd orders.

	Increment	Cumulative sum
$\Delta E(\mathrm{MP2})$	-0.2040	-0.2040
$\Delta E(\mathrm{MP3})$	-0.0068	-0.2108
$\Delta E(\mathrm{MP4})$	-0.0052	-0.2160
ΔE_{corr}		-0.2170

5.310

Convergence toward FCI for H_2O (cc-pVDZ)

CI Method	Energy [a.u.]
CISD	-76.231972
CISDT	-76.234926
CISDTQ	-76.243457
CI(5)	-76.243640
CI(6)	-76.243770
CI(7)	-76.243772
CI(8)	-76.243773
CI(9)	-76.243773
FCI	-76.243773

5.311

Computational Cost

Approximation	Computational Scaling
CISD	N^6
CISDT	N^8
CISDTQ	N^{10}
CI(5)	N^{12}
⋮	⋮
FCI	–

5.312

Standard Coupled-Cluster Approaches

Truncation of the cluster operator T:

Operator	Method	Cost
$T = T_1 + T_2$	CCSD	N^6
$T = T_1 + T_2 + T_3$	CCSDT	N^8
$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	N^{10}
$T = T_1 + T_2 + \cdots + T_N$	FCI	–

5.313

Accuracy of Coupled-Cluster Methods

- Calculations for the CO molecule using the cc-pVDZ basis set with frozen-core (FC) orbitals.
- Deviations from the FCI energy:

$$E(\mathrm{FCI}) = -113.055853 \text{ a.u.}$$

Method	CI [mH]	CC [mH]
SD	30.804	12.120
SDT	21.718	1.009
SDTQ	1.775	0.061
SDTQP	0.559	0.008
SDTQPH	0.035	0.002

5.314

Accuracy of Triple-Excitation Approximations

Method	Deviation from FCI [mH]	from CCSDT [mH]
CCSD	12.12	11.11
CCSDT-1	0.13	-0.88
CCSDT-2	1.52	0.51
CCSDT-3	1.47	0.46
CC3	0.12	-0.89
CCSD(T)	1.47	0.46
CCSD+T	-0.05	-1.06

- Calculations performed for the CO molecule using the cc-pVDZ basis with frozen core (FC).

5.315

High-Accuracy Methods – HEAT [13]

Atomization energy of CO (all energies in kJ/mol) [14]

HF-SCF	730.13 (extrapolation Q56)
+ΔCCSD(T)	356.53 (extrapolation ae, 56)
+ΔCCSDT	-2.37 (extrapolation fc, TQ)
+ΔCCSDTQ	2.22 (fc, cc-pVDZ)
+ΔCCSDTQP	0.13 (fc, cc-pVDZ)
+scalar relativistic effects	-0.65 (CCSD(T)/aug-cc-pCVTZ)
+spin–orbit splitting	-1.20 (MRCISD/cc-pVDZ+PP)
+ZPE (anharmonic)	-12.99 (CCSD(T)/cc-pVQZ)
+DBOC	0.02 (CCSD/aug-cc-pCVQZ)
Total (theory)	1071.83
Experiment	1072.13 ± 0.09

5.316

Statistical Assessment of the HEAT Method

- High-accuracy Extrapolated Ab-initio Thermochemistry (HEAT)
- Atomization energies for selected molecules (N_2, H_2, F_2, CO, O_2, etc., in kJ/mol)

Mean error	Maximum error	RMS error
-0.24	0.87	0.42

5.317

Accuracy of Geometrical Parameters in Coupled-Cluster Methods

- Computed O–H bond length $r(\mathrm{OH})$ in H_2O (in Å)

Method	CI	CC
SD	0.96131	0.96435
SD(T)	–	0.96575
SDT	0.96251	0.96583
SDTQ	0.96593	0.96614
SDTQP	0.96606	0.96616
SDTQPH	0.96616	0.96616
FCI	0.96616	

- Calculations performed using the cc-pVDZ basis set.

5.318

Standard Coupled-Cluster (CC) Approaches

Operator	Method	Scaling
$T = T_1 + T_2$	CCSD	N^6
$T = T_1 + T_2 + T_3$	CCSDT	N^8
$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	N^{10}
$T = T_1 + T_2 + T_3 + T_4 + T_5$	CCSDTQP	N^{12}
$\vdots$	$\vdots$	$\vdots$
$T = T_1 + T_2 + \cdots + T_N$	FCI	Full solution

- CCSD and CCSD(T) implementations are available in, e.g., **ACES2, ACES3, CFOUR, DALTON, GAUSSIAN, GAMESS, MOLCAS, MOLPRO, NWCHEM, ORCA, PSI, PySCF, Q-CHEM, TURBOMOLE** .
- CCSDT implementations: **ACES2, CFOUR, NWCHEM** .
- CCSDT(Q) and CCSDTQ implementations: **CFOUR, MRCC** .

5.319

Why Statistical Thermodynamics?

Quantum chemistry provides the energies of *individual molecules*, whereas thermodynamics describes *macroscopic systems* containing approximately

$$N_A = 6.022 \times 10^{23} \quad \text{molecules}$$

Statistical thermodynamics provides the connection between *microscopic energy levels* and *macroscopic thermodynamic properties*.

The central quantity is the partition function.

$$\boxed{q = \sum_i g_i e^{-E_i/kT}}$$

5.320

The Boltzmann Distribution

Consider a system in thermal equilibrium at temperature T.
Let P_i denote the probability of finding the system in quantum state i with energy E_i.
According to the Boltzmann distribution:

$$P_i = \frac{g_i e^{-E_i/kT}}{q} \quad \text{where} \quad q = \sum_i g_i e^{-E_i/kT}$$

is the partition function and g_i is the degeneracy of state i.

The ratio of populations of two states is therefore

$$\frac{P_j}{P_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/kT}$$

Higher-energy states become increasingly populated as the temperature rises.

5.321

[13] Tajti et al., J. Chem. Phys. 121, 11599 (2004)
[14] Harding et al., J. Chem. Phys. 128, 114111 (2008)

Consider a two-level system

$$\frac{P_1}{P_0} = e^{-\Delta E/kT}$$

For

$$\Delta E = 1000 \text{ cm}^{-1}$$

at $T = 298$ K,

$$\frac{P_1}{P_0} \approx 0.008$$

so less than 1% of molecules occupy the excited state.

5.322

The Partition Function

The molecular partition function is

$$q = \sum_i g_i e^{-E_i/kT}$$

It serves as a normalization constant for the Boltzmann distribution and contains all thermodynamic information about the system.

For independent molecular motions:

$$q = q_{trans} q_{rot} q_{vib} q_{elec}$$

Within the rigid rotor harmonic oscillator (RRHO) approximation:

- translation = ideal gas
- rotation = rigid rotor
- vibration = harmonic oscillator
- electronic excited states neglected

5.323

Thermodynamic Functions from the Partition Function

For one mole of molecules:

$$U = RT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

$$S = R \ln q + RT \left(\frac{\partial \ln q}{\partial T} \right)_V$$

$$H = U + RT$$

$$G = H - TS$$

All thermodynamic corrections reported by quantum chemistry programs originate from these expressions.

5.324

Translational Contribution
For an ideal gas

$$q_{trans} = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

Thermodynamic contributions:

$$U_{trans} = \frac{3}{2}RT$$

$$H_{trans} = \frac{5}{2}RT$$

$$S_{trans} = R\left[\ln q_{trans} + \frac{5}{2}\right]$$

Translation is usually the largest source of entropy. 5.325

Rotational Contribution
For a nonlinear molecule

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2}\sqrt{I_A I_B I_C}$$

where

- I_A, I_B, I_C are principal moments of inertia
- σ is the rotational symmetry number (1 for C_1 and $C_{\infty v}$, 2 for C_{2v}, 3 for C_{3v}, 12 for T_d and D_{6h}.

Thermal contributions:

$$U_{rot} = \frac{3}{2}RT$$

$$S_{rot} = R(\ln q_{rot} + 3/2)$$

5.326

Vibrational Partition Function
Each normal mode is treated as an independent quantum harmonic oscillator.

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$

Single-mode partition function:

$$q_i = \frac{\exp(-h\nu_i/2kT)}{1-\exp(-h\nu_i/kT)}$$

Total vibrational partition function:

$$q_{vib} = \prod_i q_i$$

5.327

Zero-Point Vibrational Energy
Even at absolute zero the vibrational energy is not zero:

$$E_{ZPVE} = \sum_i \frac{1}{2} h\nu_i$$

For a nonlinear molecule:

$$i = 1, \ldots, 3N-6$$

Therefore

$$E_0 = E_{el} + E_{ZPVE}$$

This is usually the first correction added to the electronic energy. 5.328

Thermal Vibrational Correction
The vibrational contribution to internal energy is

$$U_{vib} = \sum_i \left[\frac{1}{2} h\nu_i + \frac{h\nu_i}{\exp(h\nu_i/kT) - 1} \right]$$

The first term corresponds to ZPVE.
The second term describes thermal population of excited vibrational states.

High-frequency vibrations contribute very little at room temperature. 5.329

Vibrational Entropy
For a harmonic oscillator

$$S_i = R \left[\frac{x_i}{e^{x_i} - 1} - \ln\left(1 - e^{-x_i}\right) \right]$$

where

$$x_i = \frac{h\nu_i}{kT}$$

Low-frequency vibrations dominate entropy.

This is the main source of errors in the RRHO approximation. 5.330

RRHO Thermochemistry in Quantum Chemistry
The thermodynamic corrections reported by most quantum-chemical programs are derived from the same statistical-mechanical framework:

$$q = q_{trans} q_{rot} q_{vib} q_{elec}$$

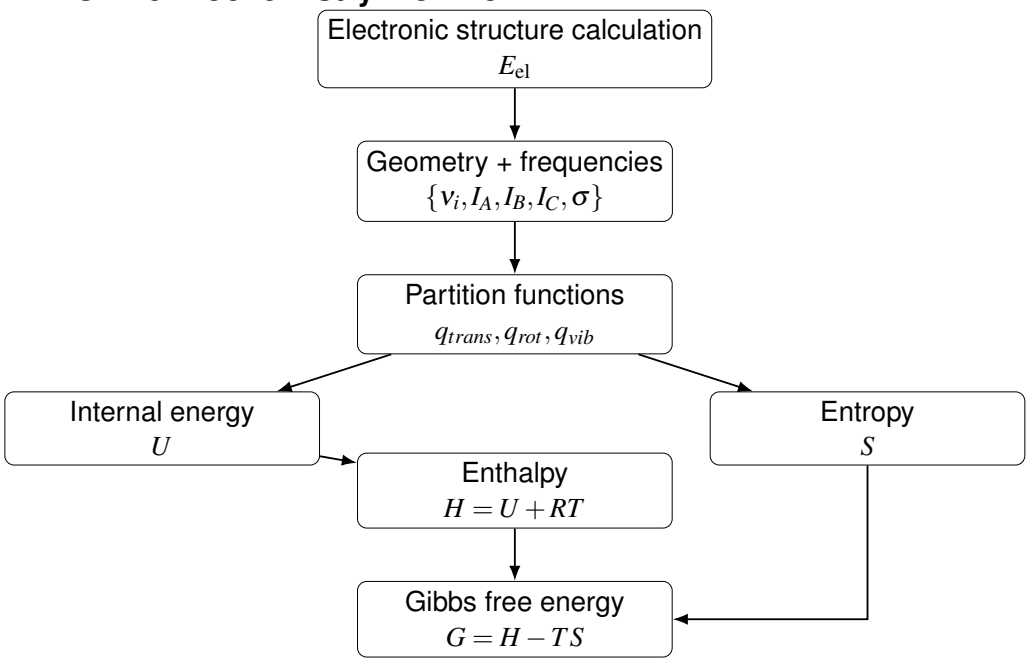
using the ideal-gas translation, rigid-rotor rotation, harmonic-oscillator vibrations and Born–Oppenheimer electronic energies.
Frequency calculations provide zero-point vibrational energy (ZPVE), thermal corrections to internal energy, and enthalpy, entropy and, hence, Gibbs free energy.

The final thermodynamic quantities are obtained as:

$$
\begin{aligned}
U(T) &= E_{el} + E_{thermal} \\
H(T) &= U(T) + RT \\
G(T) &= H(T) - TS
\end{aligned}
$$

5.331

RRHO Thermochemistry Workflow



5.332

Chapter 4
Light-matter interaction

4.333

6.1 The Jablonski diagram

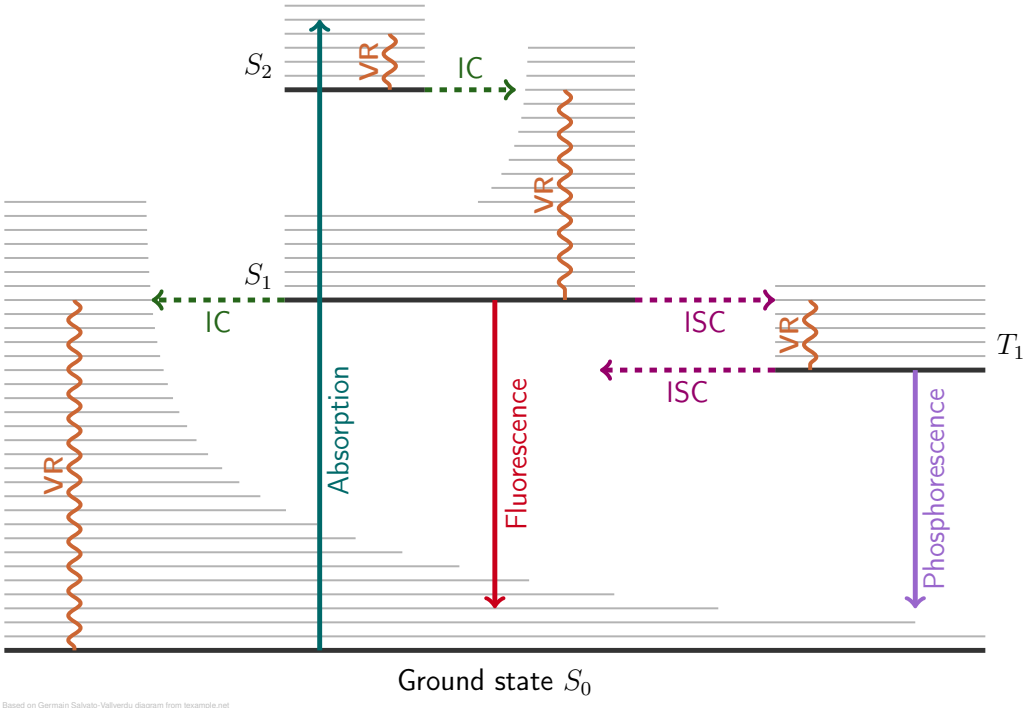


Figure 6: The Perrin–Jablonski diagram

4.334

6.2 The Golden Rule

Transition from a Single State into a Continuum
Let us consider transitions between some state $|0\rangle$ with energy E_0 and a continuum of states $|\alpha\rangle$ with energies E_α. The state $|0\rangle$ is initially populated and the transitions into the states $|\alpha\rangle$ are due to some interstate coupling expressed by $V_{0\alpha}$.

The total system is described by the following Hamiltonian

$$H = E_0|0\rangle\langle 0| + \sum_\alpha (E_\alpha|\alpha\rangle\langle\alpha| + V_{0\alpha}|0\rangle\langle\alpha| + V_{\alpha 0}|\alpha\rangle\langle 0|)$$

4.335

The transfer of occupation probability from state $|0\rangle$ decaying into a set of states $|\alpha\rangle$ can be characterized by the population of the initial state

$$P_0(t) = |\langle 0|U(t)|0\rangle|^2$$

where $U(t)$ is the time-evolution operator

$$U(t,t_0) \equiv U(t-t_0) = \exp(-iH(t-t_0)/\hbar)$$

that obeys the following equation of motion

$$i\hbar\frac{\partial}{\partial t}U(t,t_0) = HU(t,t_0)$$

with $U(t_0,t_0) = 1$

4.336

The Golden Rule of quantum mechanics

The occupation probability of the initially occupied state $|0\rangle$ decreases with time due to transitions into the manifold of states $|\alpha\rangle$. For the time evolution of $P_0(t)$ one gets a simple equation

$$\frac{d}{dt}P_0(t) = -2\Gamma P_0(t) = \frac{2\pi}{\hbar}\sum_\alpha |V_{0\alpha}|^2\delta(E_0 - E_\alpha)$$

The rate of change of the survival probability k is thus defined

$$k = 2\Gamma = \frac{2\pi}{\hbar}\sum_\alpha |V_{0\alpha}|^2\delta(E_0 - E_\alpha)$$

4.337

The Golden Rule of quantum mechanics

$$k = 2\Gamma = \frac{2\pi}{\hbar}\sum_\alpha |V_{0\alpha}|^2\delta(E_0 - E_\alpha)$$

The Dirac delta function in the rate expression can be interpreted as the energy conservation law for the transition.

Only those transitions from $|0\rangle$ to $|\alpha\rangle$ are possible for which the energy of the initial state E_0 matches some energy E_α of the final states. The rate is proportional to the square of the interstate coupling $V_{0\alpha}$.

4.338

Transition rate for a thermal ensemble
In the case of transitions between manifold of initial states $|a\rangle$ coupled to some final states $|\beta\rangle$ with energies E_β, like, for instance, in the case of nonadiabatic coupling between two electronic states in a molecule supporting the manifolds of vibrational states $\{|\alpha\rangle\}$ and $\{|\beta\rangle\}$, our system is described by the following Hamiltonian

$$H = \sum_a E_a |a\rangle\langle a| + \sum_\beta E_\alpha |\beta\rangle\langle\beta| + \sum_{\alpha\beta} (V_{\alpha\beta}|a\rangle\langle\beta| + H.c.)$$

4.339

We consider now an ensemble of systems, where the initially prepared state $|a\rangle$ may be different for each member of the ensemble. Assuming that initially the ensemble stayed in thermal equilibrium with some environment at temperature T the rate for transitions from a thermalized state manifold is

$$k_{i\to f} = \sum_a f_a k_a = \frac{2\pi}{\hbar} \sum_{\alpha\beta} f_a |V_{\alpha\beta}|^2 \delta(E_a - E_\beta)$$

where f_a is the statistical equilibrium distribution

$$f_a = \frac{\exp\{(-E_a/K_B T)\}}{\sum_{a'} \exp\{(-E_{a'}/K_B T)\}}$$

4.340

6.3 Interaction with external field

The macroscopic polarization
The key quantity of the electrostatic and electrodynamics of dielectrics is the macroscopic polarization vector $\mathbf{P}(\mathbf{X},t)$. As long as we can neglects the contributions from higher multipoles (i.e. in the long wavelength approximation) $\mathbf{P}(\mathbf{X},t)$ corresponds to the dipole density of the medium.

$$\mathbf{P}(\mathbf{X},t) = \frac{1}{\Delta V(\mathbf{X})} \sum_{m\in\Delta V} \mathbf{d}_m(t)$$

Note that in the long wavelength approximation the Hamiltonian in the Coulomb gauge is given by

$$H = H_{mol} - \hat{\mu}_m \mathbf{E}(\mathbf{X}_m, t) = H_{mol} + H^{(m)}_{field}$$

where the last term gives the molecule-field interaction in the dipole approximation.

4.341

Quantum statistical operator
The complete description of a molecular system S in an environment R is provided by the quantum-statistical operator $\hat{W}$ which in the absence of an external field becomes

$$\hat{W}_{eq} = \exp\left\{ \left(\frac{-H_{mol}}{k_B T} \right) / \mathscr{Z} \right\}$$

where $\mathscr{Z} = \int dR\, e^{-U_a/k_B T}$ is the partition function.

The time-dependent expectation value of the dipole operator can be written in two ways:

$$\mathbf{d}_m(t) = tr\{\hat{W}_{eq} U^{\dagger}(t,t_0)\hat{\mu}_m U(t,t_0)\} \equiv tr\{\hat{W}(t)\hat{\mu}_m\}$$

Alternatively the time evolution can be transfered to the statistical operator $\hat{W}(t) = U(t,t_0)\hat{W}_{eq}U^{\dagger}(t,t_0)$.

4.342

Interaction with external field
The $\hat{\mu}_m$ is the electric dipole moment operator of molecule m

$$\hat{\mu}_m = -\sum_j e\mathbf{r}_{m,j} + \sum_n e z_{m,n}\mathbf{R}_{m,n}$$

An expansion with respect to the adiabatic electronic states of the mth molecule $|\phi_{m,a}\rangle$

$$\hat{\mu}_m = \sum_{a,b} \langle\phi_{m,a}|\hat{\mu}_m|\phi_{m,b}\rangle |\phi_{m,a}\rangle\langle\phi_{m,b}|$$

leads to the *transition dipole moment* matrix elements

$$\mathbf{d}_{ab}^{(m)} = \langle\phi_{m,a}|\hat{\mu}_m|\phi_{m,b}\rangle$$

4.343

The time-dependence of the dipole operator is given by the Hamiltonian which includes the electromagnetic field via $H_{field}^{(m)}(t)$.

To arrive at the Hamiltonian we use the expression of medium electrodynamics for the interaction energy

$$E_{int} = -\int d^3\mathbf{X}\, \mathbf{E}(\mathbf{X},t)\mathbf{P}(\mathbf{X},t)$$

If we replace the various $\mathbf{d}_m$ in the expression for polarization with the related dipole moment operators one obtains the Hamiltonian for the light-matter interaction $H_{int}(t)$.

4.344

Since the external macroscopic field does not vary in a small volume element $\Delta V(\mathbf{X})$ we can incorporate $\mathbf{E}(\mathbf{X},t)$ into summation over molecules with $\mathbf{X}=\mathbf{X}_m$ being a chosen point in the mth molecule. After carring out volume integration it follows that

$$H_{int}(t)=\sum_m H^{(m)}_{field}(t)$$

with

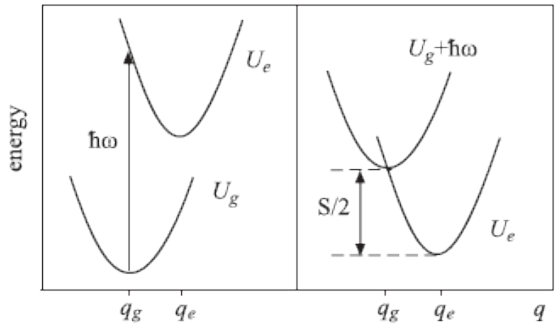
$$H^{(m)}_{field}(t)=-\mathbf{E}(\mathbf{X}_m,t)\hat{\mu}_m$$

where the various $H^{(m)}_{field}(t)$ describe the coupling of the mth molecule located at $\mathbf{X}_m$ with the external field.

4.345

6.4 One-photon absorption

Rate of transition due to one-photon absorption



Let us establish the rate $k_{g\to e}$ of transitions between the electronic ground state $|\phi_g\rangle$ and some excited state $|\phi_e\rangle$ due to the absorption of a single photon of frequency ω.

The Golden Rule formula implies that the coupling between both states is weak and that any coherence between the initial and final states is suppressed. The absorption process is viewed as the transition from the initial state $|\phi_g\rangle|\chi_{gM}\rangle$ with energy levels $\hbar\omega+E_{gM}$ to the final states $|\phi_e\rangle|\chi_{eN}\rangle$ with energy levels E_{eN} In other words, the energy of the absorbed photon $\hbar\omega$ is incorporated by defining the PES for the initial state as $U_g+\hbar\omega$.

4.346

The molecular Hamiltonian for such a two-level system, neglecting nonadiabaic couplings and including the interaction with external field

$$H(t) = \mathscr{H}_0 + \mathscr{H}_1(t)$$

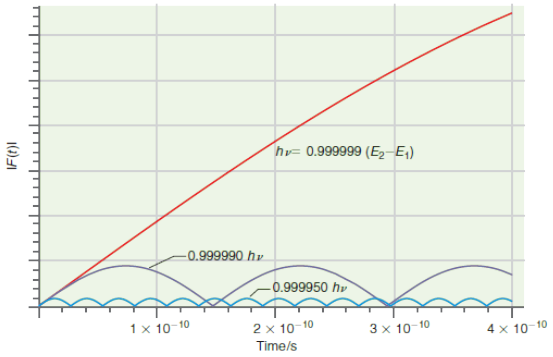
with

$$\begin{aligned}\mathscr{H}_0 =& -\hbar\omega|\phi_g\rangle\langle\phi_g| \\ \mathscr{H}_1(t) =& (H_g(q)+\hbar\omega)|\phi_g\rangle\langle\phi_g| + H_e(q)|\phi_e\rangle\langle\phi_e| \\ & -\mathbf{E}(t)(\mathbf{d}_{eg}|\phi_e\rangle\langle\phi_g| + H.c.)\end{aligned}$$

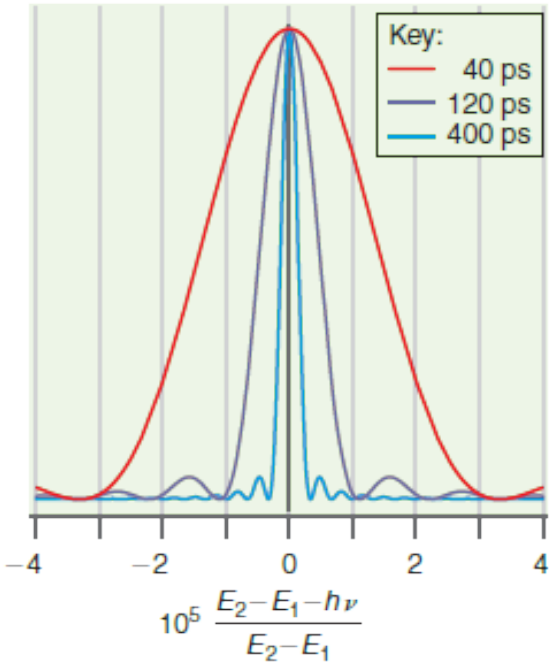
the desired transition rate is

$$k_{g\to e}\frac{2\pi}{\hbar}\sum_{M,N} f_{gM}|\langle\chi_{gM}|\mathbf{E}_0^*\mathbf{d}_{eg}^*|\chi_{eN}\rangle|^2\delta(\hbar\omega + E_{gM} - E_{eN})$$

where f_{gM} is the Boltzmann distribution factor.



The probability of finding the atom or molecule in the excited state increases nearly linearly with time for small values of t if $E_2 - E_1$ is extremely close to $\hbar\omega$. However, for photon energies that deviate even by 1 ppm from this limit, the probaility amplitude will oscillate and remain small.



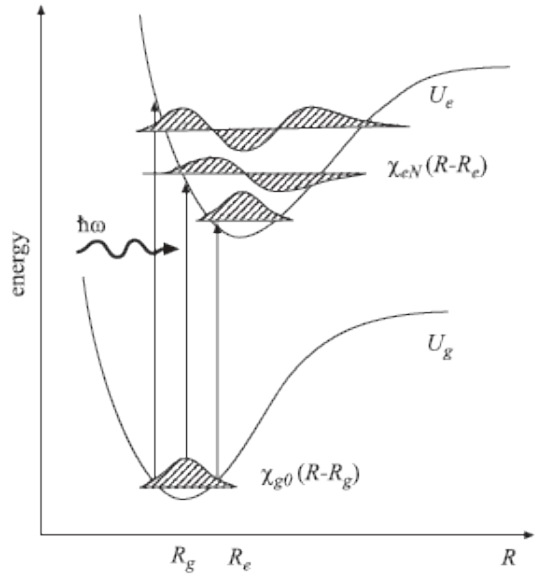
Graph of probability density in the final state against $(E_2 - E_1 - \hbar\omega)/(E_2 - E_1)$. The range of shown in the graph is only 80 parts per million of $E_2 - E_1$. The broadest and narrowest resonances are observed for $t = 40$ and $t = 400$ps, respectively. The intermediate resonance is for $t = 120$ps. All curves have been normalized to the same amplitude. Because probability amplitude increases linearly with time at resonance, probability density (related to intensity) in the final state increases as t^2 at resonance.

Often, one simplifies the matrix elements $\langle \chi_{gM} | d_{eg} | \chi_{eN} \rangle$ (d_{eg} being the scalar product of the transition dipole matrix element with the external field for a particular orientation) with $d_{eg} \langle \chi_{gM} | \chi_{eN} \rangle$.

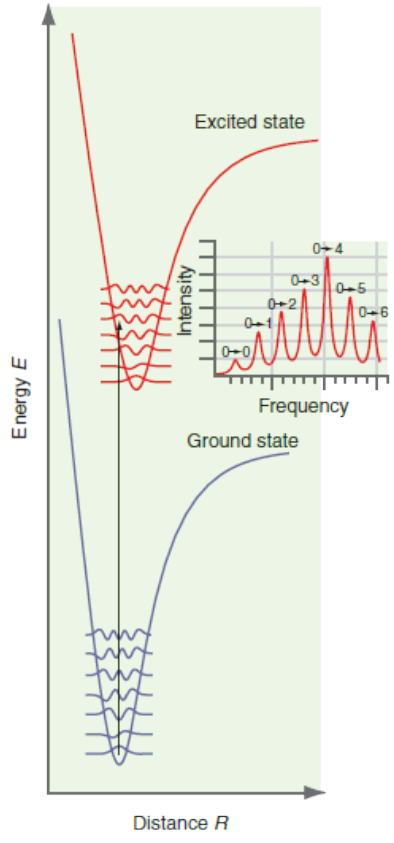
This is known as the *Condon approximation* in which the transition strength is proportional to the square of a product of pure electronic matrix element d_{eg} and the Franck–Condon factor $\langle \chi_{gM} | \chi_{eN} \rangle$ which is a zeroth-order term of the following *Herzberg–Teller expansion*.

$$\langle \chi_{gM} | d_{eg} | \chi_{eN} \rangle = d_{eg}(q_\xi^{(g)}) \langle \chi_{gM}(q_\xi) | \chi_{eN}(q_\xi) \rangle + \sum_\xi \left(\frac{\partial d_{eg}}{\partial q_\xi} \right) \langle \chi_{gM}(q_\xi) | q_\xi | \chi_{eN}(q_\xi) \rangle + \ldots$$

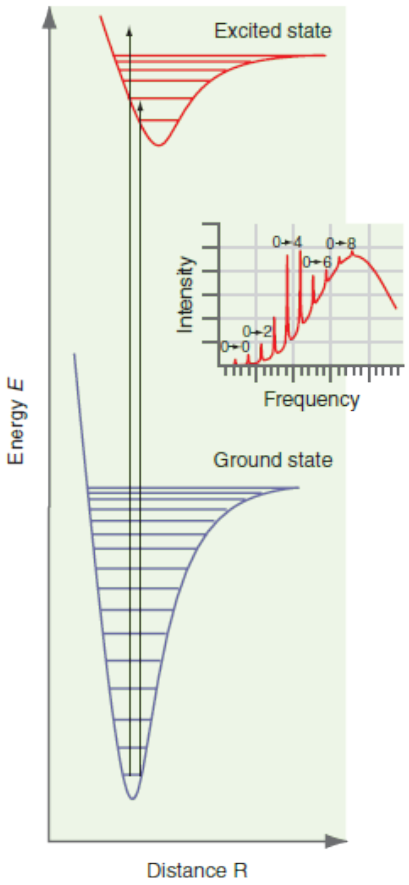
4.350



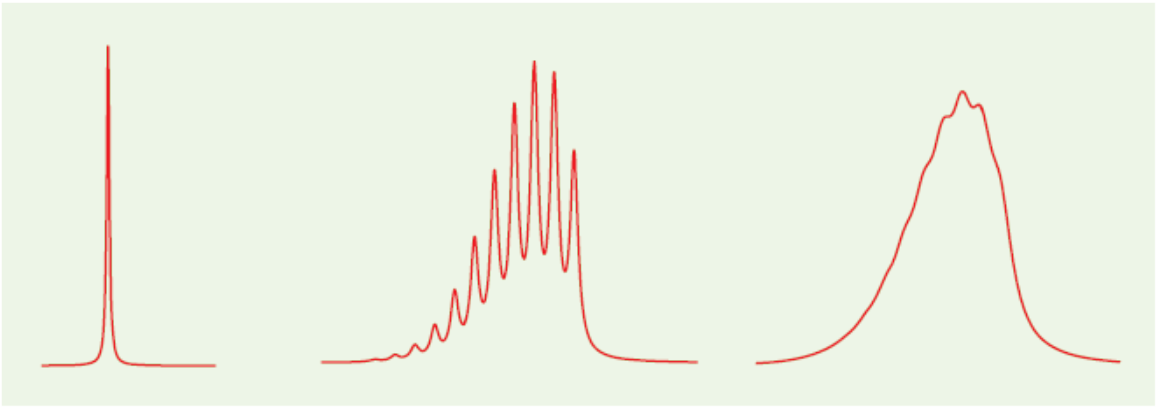
Ground and excited state PESs of a diatomic molecule are shown versus bond distance. Different vibrational states in both electronic states, together with the respective wave function, are sketched. Transitions to the excited electronic state are possible for different values of the bond length R.



The lowest vibrational energy levels and the corresponding wave functions are shown. The vertical line shows the most probable transition predicted by the Franck–Condon principle. The inset shows the relative intensities of different vibrational lines in an absorption spectrum for the potential energy curves shown.



For absorption from the ground vibrational state of the ground electronic state to the excited electronic state, a continuous energy spectrum will be observed for sufficiently high photon energy. A discrete energy spectrum is observed for smaller incident light frequencies.



The intensity of absorption in a small part of the UV-visible range of the electromagnetic spectrum is shown schematically for (a) an atom, (b) a diatomic molecule, and (c) a polyatomic molecule.

4.354

Mirror image rule for fluorescence spectra

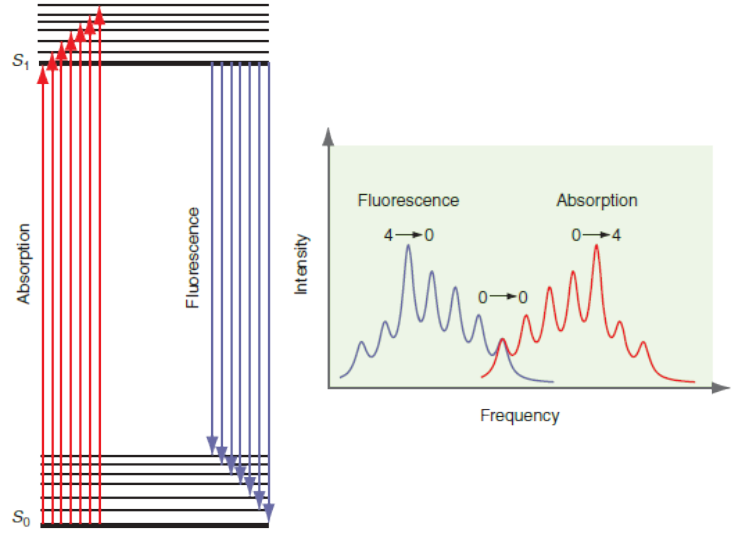
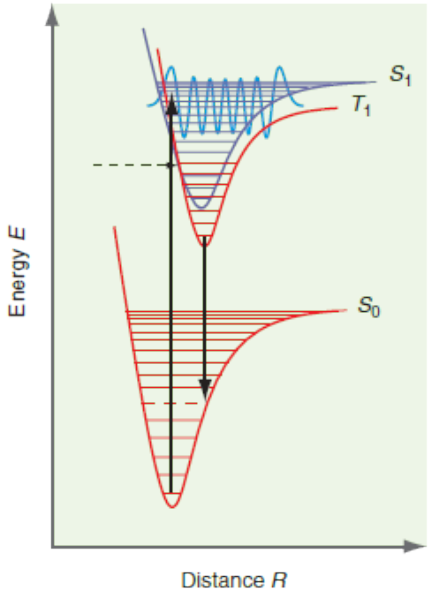


Illustration of the absorption and fluorescence bands expected if internal conversion is fast relative to fluorescence ($\tau \approx 10$ns). The relative intensities of individual transitions within the absorption and fluorescence bands are determined by the Franck-Condon principle.

4.355

Intersystem crossing and phosphorescence

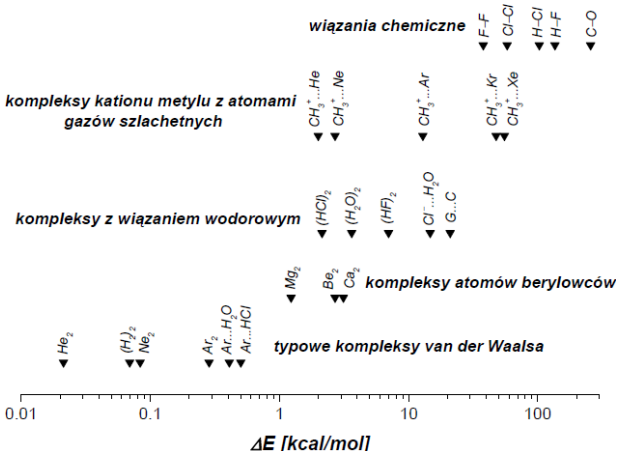


Process giving rise to phosphorescence illustrated for a diatomic molecule. Absorption from S_0 leads to a population of excited vibrational states in S_1. The molecule has a finite probability of making a transition to an excited vibrational state of T_1 if it has the same geometry in both states and if there are vibrational levels of the same energy in both states. The dashed arrow indicates the coincidence of vibrational energy levels in T_1 and S_1. For reasons of clarity, only the lowest vibrational levels in T_1 are shown. The initial excitation to S_1 occurs to a vibration state of maximum overlap with the ground state of S_0 as indicated by the blue vibrational wave function.

Chapter 7
Intermolecular Interactions

7.357

7.1 Intermolecular Interactions



Covalent bonds that hold atoms together within a molecule are relatively strong, providing thermodynamic stability over a typically very broad temperature range. However, the forces with which molecules interact with one another appear to be negligibly small. For example, the enthalpy of formation of hydrogen chloride is 431 kJ/mol, whereas its enthalpy of sublimation is only 18 kJ/mol. Nevertheless, these interactions are responsible for many macroscopic properties of matter, including the existence of its different phases.

7.358

Interaction Energy

The interaction energy between molecules A and B can be defined as

$$\Delta E\left(R,\xi,\Xi_A,\Xi_B\right) = E_{AB}\left(R,\xi,\Xi_A,\Xi_B\right) - E_A\left(\Xi_A\right) - E_B\left(\Xi_B\right)$$

where R denotes the intermolecular distance, Ξ the internal coordinates of the interacting subsystems, and ξ the set of angles defining their mutual orientation in space.

Given the weakness of the interaction, it can be treated as a small perturbation of the isolated subsystems. The interaction energy can then be calculated using perturbation theory, assuming that exact solutions for the monomers are known:

$$\Delta E = \langle \psi^0 | \hat{V} \psi \rangle$$

where the zeroth-order wavefunction Ψ^0 is constructed from the known solutions of the monomers, and $\hat{V}$ is the perturbation operator (in this case, the interaction operator) with respect to which Ψ is expanded.

7.359

Polarization Perturbation Theory

A key contribution to the understanding of weak intermolecular interactions was London's theory published in 1930. Within the perturbation-theoretical framework employed by London, the Schrödinger equation for an interacting system consisting of particles A and B can be written as

$$\left(\hat{H}^0 + \lambda \hat{V}\right) \psi_{AB} = E_{AB} \psi_{AB}$$

where the unperturbed Hamiltonian is taken as the sum of the Hamiltonians of the isolated molecules,

$$\hat{H}^0 = \hat{H}_A + \hat{H}_B$$

and the zeroth-order wavefunction is assumed to have the product form

$$\psi^0 = \psi_A \psi_B$$

Assuming the so-called intermediate normalization

$$\langle \psi_{AB} | \psi^0 \rangle = 1$$

the interaction energy can be expressed in the form of the Bloch equation

$$\Delta E = \langle \psi^0 | \lambda \hat{V} \psi_{AB} \rangle$$

7.360

Electrostatic Component of the Interaction Energy

In first-order perturbation theory we obtain the electrostatic interaction energy between the unperturbed subsystems:

$$E_{pol}^{(1)} = \langle \psi_A \psi_B | \hat{V} \psi_A \psi_B \rangle = E_{el}^{(1)}$$

Using the multipole expansion of the interaction operator:

$$\hat{V} = \frac{q_A q_B}{R} - \frac{q_A \mu_{Bz} - q_B \mu_{Az}^2}{R^2} + \frac{\mu_{Ax}\mu_{Bx} + \mu_{Ay}\mu_{By} - 2\mu_{Az}\mu_{Bz}}{R^3} + \ldots$$

we obtain the leading contributions describing interactions between point multipole moments:

$$E_{el}^{(1)} = \frac{q_A q_B}{R} + \frac{q_B \mu_{Az} - q_A \mu_{Bz}^2}{R^2} + \frac{\mu_{Ax}\mu_{Bx} + \mu_{Ay}\mu_{By} - 2\mu_{Az}\mu_{Bz}}{R^3} + \ldots$$

where for molecule A, q_A denotes its charge and μ_{Az} is the expectation value of the dipole moment along the z axis common to both subsystems.

7.361

$$V_{el} = \frac{1}{2} \int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

7.362

$$
\begin{aligned}
V_{el} \approx & \, T q^A q^B + T_\alpha \left(q^A \mu_\alpha^B - \mu_\alpha^A q^B \right) \\
& + T_{\alpha\beta} \left(q^A \Theta_{\alpha\beta}^B + \Theta_{\alpha\beta}^A q^B - \mu_\alpha^A \mu_\alpha^B \right) \\
& + T_{\alpha\beta\gamma} \left(q^A \Omega_{\alpha\beta\gamma}^B - \Omega_{\alpha\beta\gamma}^A q^B - \mu_\alpha^A \Theta_{\beta\gamma}^B + \Theta_{\beta\gamma}^A \mu_\alpha^B \right) + \ldots
\end{aligned}
$$

where:

$$
\begin{aligned}
q = \mathbf{M}^{(0)} \quad & \int \rho(\mathbf{r}) d\mathbf{r} \\
\mu_\alpha = \mathbf{M}^{(1)} \quad & \int \rho(\mathbf{r}) \alpha d\mathbf{r} \qquad (\alpha = x,y,z) \\
\Theta_{\alpha\beta} = \mathbf{M}^{(2)} \quad & \int \rho(\mathbf{r}) \alpha\beta d\mathbf{r} \qquad (\alpha,\beta = x,y,z) \\
\Omega_{\alpha\beta\gamma} = \mathbf{M}^{(3)} \quad & \int \rho(\mathbf{r}) \alpha\beta\gamma d\mathbf{r} \qquad (\alpha,\beta,\gamma = x,y,z) \\
& \ldots
\end{aligned}
$$

$$
\begin{aligned}
\hat{T} &= \frac{1}{R} \\
\hat{T}_{\alpha\beta\cdots\omega} &= \nabla_\alpha \nabla_\beta \cdots \nabla_\omega \left(\frac{1}{R} \right)
\end{aligned}
$$

7.363

According to the Boltzmann distribution, the probability of a given orientation ω is proportional to $\exp(-\beta E(\omega))$, where $\beta = (kT)^{-1}$. The average electrostatic interaction energy (expanding the exponential factor into a series) is therefore given by:

$$
\begin{aligned}
\langle E_{el} \rangle = & \frac{\int E(\omega) \left[1 - \beta E(\omega) + \ldots \right] d\omega}{\int \left[1 - \beta E(\omega) + \ldots \right] d\omega} \\
= & \frac{q_a q_b}{R} - \frac{1}{3kT} \frac{q_a^2 \mu_b^2 + q_b^2 \mu_a^2}{R^4} - \frac{2}{3kT} \frac{\mu_a^2 \mu_b^2}{R^6} + \ldots
\end{aligned}
$$

7.364

Induction and Dispersion Interactions

The second-order correction to the interaction energy, accounting for induction and dispersion effects, may be written as the following sum over the states of the isolated subsystems labeled by the index m ($E_{X,0}$ denotes the ground-state energy of subsystem X):

$$
E_{pol}^{(2)} = - \sum_{m \neq 0} \frac{|\langle \psi^0 | \hat{V} \psi_{AB,m} \rangle|^2}{E_m - E_0} = E_{ind}^{(2)} + E_{disp}^{(2)}
$$

Using the multipole expansion of the interaction operator, we obtain the leading terms describing interactions between permanent and induced point multipole moments (the latter denoted by a tilde) in the case of induction interactions, and between moments induced by fluctuations of the electron density in the case of dispersion interactions:

$$E_{ind}^{(2)} = -\sum_{m_2 \neq 0} \frac{|-(q_A \tilde{\mu}_{Bz}) R^{-2} + (\mu_{Ax}\tilde{\mu}_{Bx} + \mu_{Ay}\tilde{\mu}_{By} - 2\mu_{Az}\tilde{\mu}_{Bz}) R^{-3} + \ldots|^2}{E_{B,m_2} - E_{B,0}}$$

$$E_{disp}^{(2)} = -\sum_{\substack{m_1 \neq 0 \\ m_2 \neq 0}} \frac{|(\tilde{\mu}_{Ax}\tilde{\mu}_{Bx} + \tilde{\mu}_{Ay}\tilde{\mu}_{By} - 2\tilde{\mu}_{Az}\tilde{\mu}_{Bz}) R^{-3} + \ldots|^2}{(E_{A,m_1} + E_{B,m_2}) - (E_{A,0} + E_{B,0})}$$

7.365

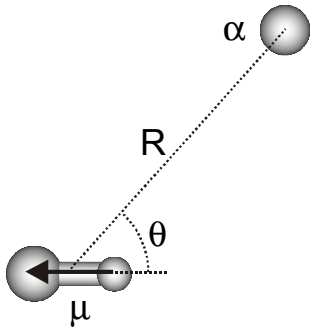
INDUCTION INTERACTIONS

The charge-density distribution of a molecule placed in an external electric field F is modified. For a homogeneous field, the induced dipole moment may be expressed as the following expansion:

$$\tilde{\mu} = \alpha_{\alpha\beta} F_\beta + \frac{1}{2}\beta_{\alpha\beta\gamma} F_\beta F_\gamma + \frac{1}{6}\gamma_{\alpha\beta\gamma\delta} F_\beta F_\gamma F_\delta + \ldots$$

7.366

Consider the long-range interaction between a polar molecule (e.g., HF) and a noble-gas atom (e.g., He). For large values of R, assuming a linear response and taking into account the isotropy of the He atom,



$$\tilde{\mu} = \alpha F$$

and the interaction energy becomes

$$E_{ind} = -\int_0^F \tilde{\mu}\, dF = -\int_0^F \alpha F\, dF = -\frac{1}{2}\alpha F^2$$

7.367

For the case considered, the magnitude of the electric field generated by the dipole moment μ is:

$$F(R,\theta) = \frac{\sqrt{1+3\cos^2\theta}}{4\pi\varepsilon_0}\frac{\mu}{R^3}$$

Hence, the dipole–induced dipole interaction energy for a given orientation is

$$E_{ind} = -\frac{1+3\cos^2\theta}{2(4\pi\varepsilon_0)^2}\frac{\alpha\mu^2}{R^6}$$

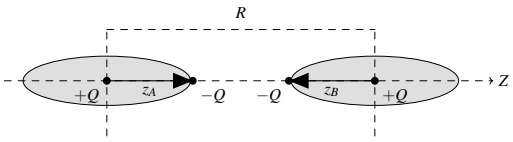
and, after orientational averaging,

$$\langle E_{ind} \rangle = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\alpha\mu^2}{R^6}$$

7.368

DISPERSION INTERACTIONS

Consider the interaction between two inert atoms, A and B. Each atom is represented as an electron of mass m bound by a harmonic potential with force constant k:



$$H_A = \frac{p_A^2}{2m} + \frac{1}{2}kx_A^2.$$

Fluctuations of the electron density generate instantaneous dipole moments along the intermolecular axis, which then interact with one another:

$$\mathscr{H} = \frac{1}{2m}\left(p_A^2 + p_B^2\right) + \frac{1}{2}k\left(x_A^2 + x_B^2 + 2cx_Ax_B\right)$$

where c is a coupling constant proportional to R^{-3}. 7.369

The Hamiltonian may be separated into two uncoupled oscillators corresponding to the normal vibrations $x_A \pm x_B$:

$$\begin{aligned}\mathscr{H} = &\frac{1}{4m}\left(p_A + p_B\right)^2 + \frac{1}{4}k\left(1+c\right)\left(x_A + x_B\right)^2 \\ &+ \frac{1}{4m}\left(p_A - p_B\right)^2 + \frac{1}{4}k\left(1-c\right)\left(x_A - x_B\right)^2\end{aligned}$$

with frequencies

$$\omega_\pm = \omega_0\sqrt{1 \pm c},$$

where

$$\omega_0 = \sqrt{k/m}$$

is the vibrational frequency of the isolated atoms. The corresponding zero-point vibrational energy is

$$\frac{1}{2}\hbar\left(\omega_+ + \omega_-\right).$$

7.370

The zero-point vibrational energy becomes:

$$\begin{aligned}\frac{1}{2}\hbar\left(\omega_+ + \omega_-\right) &= \frac{1}{2}\hbar\omega_0\left(\sqrt{1+c} + \sqrt{1-c}\right) \\ &= \frac{1}{2}\hbar\omega_0\left(2 - \frac{1}{4}c^2 - \frac{5}{64}c^4 - \ldots\right)\end{aligned}$$

The energy lowering relative to the zero-point energy of the separated atoms ($\hbar\omega_0$) is therefore

$$E_{disp} = -\hbar\omega_0\left(\frac{1}{8}c^2 + \frac{5}{128}c^4 + \ldots\right).$$

7.371

EXCHANGE REPULSION

The product wavefunction ψ^0 is not antisymmetric with respect to the exchange of electrons between the subsystems. Although its antisymmetrization is straightforward, the function

$$\hat{\mathscr{A}}\psi_A\psi_B$$

is not an eigenfunction of $\hat{H}^0$.

To overcome this difficulty, two alternative approaches have been proposed. One modifies the construction of the zeroth-order Hamiltonian $\hat{H}^0$ so that $\hat{\mathscr{A}}\psi_A\psi_B$ becomes its eigenfunction. The second requires a reformulation of perturbation theory itself and is commonly referred to as *symmetry adaptation*. 7.372

Exchange Component of the Interaction Energy

Each correction obtained within polarization perturbation theory is accompanied by a corresponding exchange correction arising from the proper treatment of permutation symmetry:

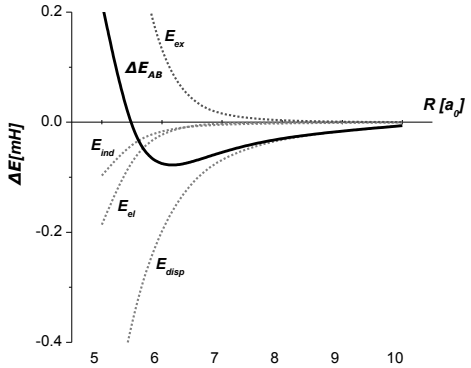
$$E^{(n)} = E^{(n)}_{pol} + E^{(n)}_{exch}$$

In first-order perturbation theory, one obtains the exchange-repulsion energy. It originates from the reduction of the electron density in the region where the subsystem wavefunctions overlap, as required by the Pauli exclusion principle, and from the associated reduction in the screening of nuclear charges:

$$E^{(1)}_{exch} = \langle \psi_A\psi_B | (\hat{V} - E^{(1)}_{el})\hat{\mathscr{A}}\psi_A\psi_B \rangle$$ 7.373

Intermolecular interactions therefore consist of four fundamental components:

- electrostatic attraction or repulsion;
- induction attraction;
- dispersion attraction; and
- exchange repulsion.



7.374

Chapter 5
Theory of nonlinear optical phenomena

5.375

8.1 Nonlinear optical properties

Bulk nonlinear optical properties
Nonlinear optical behavior manifests itself when a macroscopic observable (e.g. polarization of a medium) is induced in a sample upon its exposure to intense electromagnetic radiation, and the intensity of this effect increases nonlinearly with applied field.

$$\mathbf{P}(\mathbf{F}) = \mathbf{P}^{(\mathbf{0})} + \mathbf{X}^{(1)} \cdot \mathbf{F} + \frac{1}{2!}\mathbf{X}^{(2)} : \mathbf{FF} + \frac{1}{3!}\mathbf{X}^{(3)} \vdots \mathbf{FFF} + \dots ,$$

$\mathbf{P}(\mathbf{F})$ is the measured observable with respect to electric or magnetic field, $\mathbf{P}^{(\mathbf{0})}$ is an observable without applied perturbation and $\mathbf{X}^{(1)}$, $\mathbf{X}^{(2)}$ and $\mathbf{X}^{(3)}$ are the first-, second- and third-order macroscopic susceptibility tensors, respectively.[15]

5.376

Polarization of a medium
Considering *only the electric field* perturbation, the polarization of a medium can be put in the following form:

$$\mathbf{P}(\mathbf{F}) = \mathbf{P}^{(\mathbf{0})} + \varepsilon_0 \left[\boldsymbol{\chi}^{(1)} \cdot \mathbf{F} + \frac{1}{2!}\boldsymbol{\chi}^{(2)} : \mathbf{FF} + \frac{1}{3!}\boldsymbol{\chi}^{(3)} \vdots \mathbf{FFF} + \dots \right]$$

where ε_0 is the electrical permittivity of free space and $\boldsymbol{\chi}^{(i)}$ are the respective optical susceptibility tensors.

5.377

By substituting Fourier relation for electric field oscillation:

$$\boldsymbol{F}(t) = \sum_{\omega} \boldsymbol{F}(\omega) e^{-i\omega t}$$

to $\mathbf{P}(\mathbf{F})$ one obtains terms proportional to the multiples of the incident field frequency and the overall output polarization can be partitioned into contributions from *multiple-wave mixing terms* having its origins in *molecule-photon interactions at the microscopic level*.

5.378

[15] Generally in the nonlinear optics all tensor quantities of interest are *Cartesian* and there is no need to distinguish covariant and contravariant indices.

The respective time-dependent polarization can be then implicitly expressed by the corresponding susceptibility tensor components:[16]

$$
\begin{aligned}
P_\alpha(t) = P_\alpha^{(0)} &+ \varepsilon_0 \sum_{\omega} \chi^{(1)}_{\alpha\beta}(-\omega;\omega) F^{\omega}_{\beta} e^{-i\omega t} \\
&+ \frac{1}{2}\varepsilon_0 \sum \mathscr{P}_{1,2} \sum_{\omega_1\omega_2} \chi^{(2)}_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) F^{\omega_1}_{\beta} F^{\omega_2}_{\gamma} e^{-i\omega_\sigma t} \\
&+ \frac{1}{6}\varepsilon_0 \sum \mathscr{P}_{1,2,3} \sum_{\omega_1\omega_2\omega_3} \chi^{(3)}_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) F^{\omega_1}_{\beta} F^{\omega_2}_{\gamma} F^{\omega_3}_{\delta} e^{-i\omega_\sigma t} \\
&+ \dots
\end{aligned}
$$

5.379

A note about the symmetry

Although the total number of susceptibility or hyperpolarizability tensor elements is large,[17] the actual number of independent components can be greatly reduced:[-1ex]

- twice for real electric fields (i.e. any physical situation),
- the last $r-1$ frequency indices in the r-rank tensor can be interchanged with last $r-1$ Cartesian indices (intrinsic permutational symmetry; reduces the number twice for $\chi^{(2)}$ and six times for $\chi^{(3)}$),
- in the limit of static fields or if the susceptibilities do not depend on frequency one can freely interchange field indices as well (so called Kleinman's symmetry)

$$
\begin{aligned}
\chi^{(1)}_{ij} &= \chi^{(1)}_{ji} \qquad \text{or} \qquad \alpha_{ij} = \alpha_{ji} \\
\chi^{(2)}_{ijk} &= \chi^{(2)}_{jik} = \dots \qquad \text{or} \qquad \beta_{ijk} = \beta_{jik} = \dots
\end{aligned}
$$

- other reductions (e.g. due crystalline symmetry)

5.380

Polarization of a medium can also be expressed by Fourier series according to:

$$
\mathbf{P}(t) = \sum_n \mathbf{P}(\omega_n) e^{-i\omega_n t} = \sum_i \sum_{r=0} \mathbf{P}^{(r)}(\omega_i) e^{-i\omega_i t} \ ,
$$

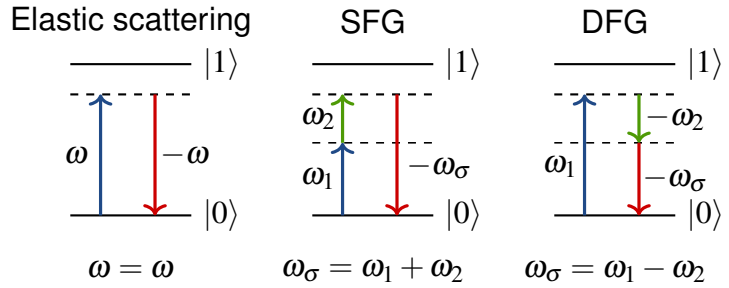
where the summation extends over all positive and negative frequencies ω_n constituting the incident electromagnetic radiation.

5.381

[16] Negative sign indicates the output and positive sign the input frequency, respectively, and the $\sum\mathscr{P}$ operator performs summation of terms obtained by permuting pairs of indices for input frequencies to impose intrinsic symmetry.

[17] 9 for $\chi^{(1)}$, 27 for $\chi^{(2)}$ and 81 for $\chi^{(3)}$

On a microscopic scale light-matter interaction can be regarded as scattering of incident photons by electronic density of a molecule.



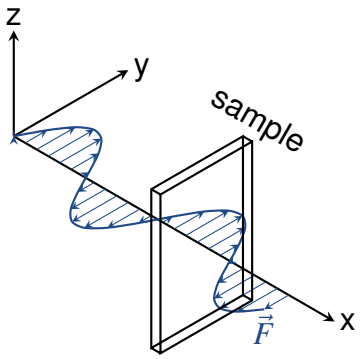
Different scenarios of photon interaction with a molecular electronic state: elastic Rayleigh scattering, sum-frequency generation (SFG), difference-frequency generation (DFG). The virtual energy levels are depicted by dashed lines.[a]

[a]The lifetime of the virtual state must conform to the time-energy uncertainty $\tau\Delta E \sim \frac{\hbar}{2}$

5.382

Classical view of light-matter interaction

In the complementary view, the coupling between the electromagnetic plane wave and molecular system can be described (to a first approximation) as a classical *electric-dipole coupling*.



5.383

Molecular (hyper)polarizabilities

The induced charge polarization depends, to first order, on linear polarizability $\boldsymbol{\alpha}$, however, in general the time dependent polarization $\boldsymbol{\mu}(t)$ can be expressed as a Taylor series in the electric field strength $\boldsymbol{F}(t)$

$$\mu_\alpha(t) = \mu_\alpha^{(0)} + \alpha_{\alpha\beta}F_\beta(t) + \frac{1}{2}\beta_{\alpha\beta\gamma}F_\beta(t)F_\gamma(t) + \\ + \frac{1}{6}\gamma_{\alpha\beta\gamma\delta}F_\beta(t)F_\gamma(t)F_\delta(t) + \ldots$$

The above equation introduces the molecular first-order hyperpolarizability $\boldsymbol{\beta}$ and second-order hyperpolarizability $\boldsymbol{\gamma}$.[a]

[a]Einstein summation convention over repeating indices shall be assumed hereafter.

5.384

8.2 Time-dependent polarization

Molecular time-dependent polarization
The electric field is vectorial and composed of static and one or more time dependent components:

$$F_\alpha(t) = \sum_\omega F_\alpha^\omega e^{-i\omega t}$$

If we put the above Fourier series into the Taylor series expansion for the time dependent polarization $\mu_\alpha(t)$ and simplify we obtain:

$$\begin{aligned}\mu_\alpha(t) = \mu_\alpha^0 &+ \sum_\omega \alpha_{\alpha\beta}(-\omega_\sigma;\omega) F_\beta^\omega e^{-i\omega t} \\ &+ \frac{1}{2}\sum_{\omega_1\omega_2} \beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) F_\beta^{\omega_1} F_\gamma^{\omega_2} e^{-i\omega_\sigma t} \\ &+ \frac{1}{6}\sum_{\omega_1\omega_2\omega_3} \gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) F_\beta^{\omega_1} F_\gamma^{\omega_2} F_\delta^{\omega_3} e^{-i\omega_\sigma t} + \ldots\end{aligned}$$

5.385

Illustrative example
Two lasers A and B operating at frequencies ω_A and ω_B generate external field:

$$F_\alpha(t) = F_\alpha^{\omega_A}\cos(\omega_A t) + F_\alpha^{\omega_B}\cos(\omega_B t)$$

Including terms up to second order in the field one obtains:

$$\begin{aligned}\mu_\alpha(t) = \mu_\alpha^0 &+ \alpha_{\alpha\beta}[F_\beta^{\omega_A}\cos(\omega_A t) + F_\beta^{\omega_B}\cos(\omega_B t)] \\ &+ \frac{1}{2}\beta_{\alpha\beta\gamma}[F_\beta^{\omega_A}\cos(\omega_A t) + F_\beta^{\omega_B}\cos(\omega_B t)]\times \\ &\quad [F_\beta^{\omega_A}\cos(\omega_A t) + F_\beta^{\omega_B}\cos(\omega_B t)]\end{aligned}$$

With the use of trigonometric identity $cos(u)cos(v) = \frac{1}{2}[cos(u+v) + cos(u-v)]$ one can rewrite the polarization as ... 5.386

$$\begin{aligned}\mu_\alpha(t) = \mu_\alpha^0 &+ \\ &\sum_{\omega\in\{\omega_A,\omega_B\}} \Big[\alpha_{\alpha\beta}(-\omega;\omega) F_\beta^\omega \cos(\omega t) + \frac{1}{2}\beta_{\alpha\beta\gamma}(0;\omega,-\omega) F_\beta^\omega F_\gamma^\omega \\ &+ \frac{1}{2}\beta_{\alpha\beta\gamma}(-2\omega;\omega,\omega) F_\beta^\omega F_\gamma^\omega \cos(2\omega t)\Big] \\ &+ \beta_{\alpha\beta\gamma}(-(\omega_A+\omega_B);\omega_A,\omega_B) F_\beta^{\omega_A} F_\gamma^{\omega_B} \cos([\omega_A+\omega_B]t) \\ &+ \beta_{\alpha\beta\gamma}(-(\omega_A-\omega_B);\omega_A,-\omega_B) F_\beta^{\omega_A} F_\gamma^{\omega_B} \cos([\omega_A-\omega_B]t)\end{aligned}$$

5.387

8.3 Nonlinear optical processes

Process	Frequencies
	Second order processes
Static	$0;0,0$
Electro-optical Pockels effect (EOPE)	$-\omega;\omega,0$
Second harmonic generation (SHG)	$-2\omega;\omega,\omega$
Optical rectification (OR)	$0;\omega,-\omega$
Sum frequency generation (SFG)	$-\omega_3;\omega_1,\omega_2$
Difference frequency generation (DFG)	$-\omega_3;\omega_1,\omega_2$
	Third order processes
Static	$0;0,0,0$
Electro-optical Kerr effect (EOKE)	$-\omega;\omega,0,0$
Intensity dependent refractive index (IDRI)	$-\omega;\omega,-\omega,\omega$
Electric field induced SHG (ESHG)	$-2\omega;\omega,\omega,0$
Third harmonic generation (THG)	$-3\omega;\omega,\omega,\omega$
Electric field induced OR (EFIOR)	$-\omega;0,0,\omega$
Four–wave SFG	$-\omega_4;\omega_1,\omega_2,\omega_3$
Four–wave DFG	$-\omega_4;\omega_1,\omega_2,\omega_3$

Table 1: Selected nonlinear optical processes

5.388

8.4 Time-dependent perturbation theory

Time dependent Schrödinger equation
The time evolution of the state vector is given by the time dependent Schrödinger equation:

$$i\hbar\frac{\partial|\psi(t)\rangle}{\partial t}=\hat{H}|\psi(t)\rangle$$

where $\hat{H}$ is the Hamiltonian which may be either time-independent or time-dependent.

In the latter case, if the time-dependent part of $\hat{H}$ is just a small perturbation, it is possible to express the solution in terms of eigenstates of the unperturbed system.

5.389

The $\hat{H}$ could be then separated according to:

$$\hat{H}=\hat{H}_0+\hat{V}(t)$$

Assuming that the exact solutions for unperturbed system are known (which is hardly ever true):

$$\hat{H}_0|n\rangle=E_n|n\rangle$$

where $|n\rangle$ is the exact vibronic eigenstate and E_n is the corresponding energy, the molecular state can be expressed as:

$$|\psi(t)\rangle = \sum_n^\infty c_n(t)|n\rangle$$

where $c(-\infty) = \delta_{0n}$ as that system is assumed to be in its ground state before perturbation. 5.390

In the absence of perturbation:

$$c_n(t) = c_n(0)\exp(-iE_nt/\hbar)$$

Thus, it is appropriate to rewrite the state vector as:

$$|\psi(t)\rangle = \sum_n^\infty d_n(t)e^{-iE_nt/\hbar}|n\rangle$$

The task of finding the unknown function $d_n(t)$ could be simplified by expanding it into power series with respect to the perturbation:

$$d_n(t) = d_n^{(0)} + d_n^{(1)}(t) + d_n^{(2)}(t) + \ldots$$

where $d_n^{(0)}$ is time-independent to ensure the proper solution for zero-perturbation condition. 5.391

Operating on both sides of equation for the state vector with $i\hbar\frac{\partial}{\partial t} - \hat{H}$ and multiplying with the bra vector $\langle m|\exp(iE_mt/\hbar)$ (both from the left) gives an equation for $d_m(t)$:

$$\frac{\partial d_m^{(N)}}{\partial t} = -i\hbar^{-1}\sum_n^\infty \langle m|\hat{V}(t)|n\rangle e^{i\omega_{mn}t} d_n^{(N-1)}$$

where ω_{mn} is the transition frequency $(E_m - E_n)/\hbar$ and $d_n^{(0)}$ is equal to δ_{0n}. Thus we obtained a recursive equation in which the next order response $d_m^{(N)}$ is obtained by feeding it with the previous one $d_m^{(N-1)}$ by time-integration. 5.392

It is customary to put the wave function in the following expansion:

$$|\psi(t)\rangle = |\psi^{(0)}(t)\rangle + |\psi^{(1)}(t)\rangle + \ldots$$

where the corrections are given by:

$$|\psi^{(N)}(t)\rangle = \sum_n^\infty d_n^{(N)}e^{-iE_nt/\hbar}|n\rangle$$

5.393

The expectation value of $\hat{\mu}$ thus becomes:

$$\langle\psi(t)|\hat{\mu}|\psi(t)\rangle = \langle\hat{\mu}^{(0)}\rangle + \langle\hat{\mu}^{(1)}\rangle + \langle\hat{\mu}^{(2)}\rangle + \langle\hat{\mu}^{(3)}\rangle\ldots$$

where:

$$\begin{aligned}
\langle\hat{\mu}^{(0)}\rangle &= \langle\psi^{(0)}|\hat{\mu}|\psi^{(0)}\rangle \\
\langle\hat{\mu}^{(1)}\rangle &= \langle\psi^{(0)}|\hat{\mu}|\psi^{(1)}\rangle + \langle\psi^{(1)}|\hat{\mu}|\psi^{(0)}\rangle \\
\langle\hat{\mu}^{(2)}\rangle &= \langle\psi^{(0)}|\hat{\mu}|\psi^{(2)}\rangle + \langle\psi^{(1)}|\hat{\mu}|\psi^{(1)}\rangle + \langle\psi^{(2)}|\hat{\mu}|\psi^{(0)}\rangle \\
\langle\hat{\mu}^{(3)}\rangle &= \langle\psi^{(0)}|\hat{\mu}|\psi^{(3)}\rangle + \langle\psi^{(1)}|\hat{\mu}|\psi^{(2)}\rangle + \langle\psi^{(2)}|\hat{\mu}|\psi^{(1)}\rangle + \\
&\quad \langle\psi^{(3)}|\hat{\mu}|\psi^{(0)}\rangle
\end{aligned}$$

5.394

First-order response

In the electric dipole approximation the interaction between molecule and the electric field is given by:[18]

$$\hat{V}(t) = -\hat{\mu}_\alpha F_\alpha(t) e^{\varepsilon t}$$

Inserting $\hat{V}(t)$ and $d_n^{(0)}$ into equation for $d_m(t)$ and integrating over time one obtains the first-order response:

$$\begin{aligned} d_m^{(1)} &= i\hbar^{-1} \int_{-\infty}^{t} \sum_n^\infty \langle m|\hat{\mu}_\alpha \sum_{\omega_1} F_\alpha^{\omega_1} e^{-i\omega_1 t'} e^{\varepsilon t'} |n\rangle e^{i\omega_{mn} t'} \delta_{0n} dt' \\ &= \hbar^{-1} \sum_{\omega_1} \frac{\langle m|\hat{\mu}_\alpha|0\rangle F_\alpha^{\omega_1}}{\omega_{m0} - \omega_1 - i\varepsilon} e^{i(\omega_{m0}-\omega_1)t} e^{\varepsilon t} \end{aligned}$$

where the factor $e^{\varepsilon t}$ with the infinitesimal ε ensures that the perturbation is switched on adiabatically and vanishes for $t = -\infty$.

5.395

Finally, one gets the expression for first-order polarization:

$$\begin{aligned} \langle \hat{\mu}_\alpha^{(1)} \rangle &= \langle \psi^{(0)}|\hat{\mu}|\psi^{(1)}\rangle + \langle \psi^{(1)}|\hat{\mu}|\psi^{(0)}\rangle = \\ &= \langle 0|e^{iE_0 t/\hbar}\hat{\mu}_\alpha \\ &\times \sum_n^\infty \hbar^{-1} \sum_{\omega_1} \frac{\langle n|\hat{\mu}_\beta|0\rangle F_\beta^{\omega_1}}{\omega_{n0} - \omega_1 - i\varepsilon} e^{i(\omega_{n0}-\omega_1)t} e^{\varepsilon t} e^{-iE_n t/\hbar} |n\rangle \\ &+ \sum_n^\infty \hbar^{-1} \sum_{\omega_1} \frac{\langle 0|\hat{\mu}_\beta|n\rangle [F_\beta^{\omega_1}]^*}{\omega_{n0} + \omega_1 + i\varepsilon} e^{-i(\omega_{n0}-\omega_1)t} e^{\varepsilon t} e^{-iE_n t/\hbar} \\ &\times \langle n|\hat{\mu}_\alpha e^{-iE_0 t/\hbar}|0\rangle \\ &= \sum_{\omega_1} \hbar^{-1} \sum_n^\infty \left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\omega_{n0} - \omega_1 - i\varepsilon} + \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{\omega_{n0} + \omega_1 + i\varepsilon} \right] \\ &\times F_\beta^{\omega_1} e^{-i\omega_1 t} e^{\varepsilon t} \end{aligned}$$

and by inspection of expression for time-dependent polarization:

$$\mu_\alpha(t) = \mu_\alpha^0 + \sum_\omega \alpha_{\alpha\beta}(-\omega_\sigma;\omega) F_\beta^\omega e^{-i\omega t} + \ldots$$

5.396

One identifies linear polarizability:

$$\alpha_{\alpha\beta}(-\omega;\omega) = \frac{1}{\hbar} \sum_n^\infty \left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\omega_{n0} - \omega - i\varepsilon} + \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{\omega_{n0} + \omega + i\varepsilon} \right]$$

In the nonresonant region with reasonable laser detuning, and dealing with a set of real eigenstates $\{|n\rangle\}$ one may neglect the imaginary term:[19]

$$\alpha_{\alpha\beta}(-\omega;\omega) = \frac{1}{\hbar} \sum_n^{\infty\prime} \left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\omega_{n0} - \omega} + \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{\omega_{n0} + \omega} \right]$$

5.397

[18] Note that the field is treated classically

[19] The prime symbol in the summation indicates exclusion of the ground state

Accordingly one may derive expressions for second-order polarization:

$$\langle\hat{\mu}^{(2)}\rangle = \langle\psi^{(0)}|\hat{\mu}|\psi^{(2)}\rangle + \langle\psi^{(1)}|\hat{\mu}|\psi^{(1)}\rangle + \langle\psi^{(2)}|\hat{\mu}|\psi^{(0)}\rangle$$

and consequently the first hyperpolarizability:

$$\begin{aligned}\beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) = \\ \hbar^{-2}\sum\mathscr{P}_{1,2}\sum_{np}\left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|p\rangle\langle p|\hat{\mu}_\gamma|0\rangle}{(\omega_{n0}-\omega_\sigma-i2\varepsilon)(\omega_{p0}-\omega_2-i\varepsilon)}\right. \\ + \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|p\rangle\langle p|\hat{\mu}_\gamma|0\rangle}{(\omega_{n0}+\omega_1-i\varepsilon)(\omega_{p0}-\omega_2-i\varepsilon)} + \\ \left. + \frac{\langle 0|\hat{\mu}_\gamma|p\rangle\langle p|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{(\omega_{n0}+\omega_\sigma+i2\varepsilon)(\omega_{p0}+\omega_2+i\varepsilon)}\right]\end{aligned}$$

where the $\sum\mathscr{P}_{1,2}$ operator performs summation of terms obtained by permuting pairs (β,ω_1) and (γ,ω_2) to impose intrinsic symmetry. 5.398

8.5 Molecular (hyper)polarizabilities

Working formulas in the nonresonant region

$$\begin{aligned}\alpha_{\alpha\beta}(-\omega;\omega) &= \hbar^{-1}\sum_n{}'^{\infty}\left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\omega_{n0}-\omega} + \frac{\langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{\omega_{n0}+\omega}\right] \\ \beta_{\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2) &= \hbar^{-2}\sum\mathscr{P}_{-\sigma,1,2}\sum_{np}{}'\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\bar{\mu}}_\beta|p\rangle\langle p|\hat{\mu}_\gamma|0\rangle}{(\omega_{n0}-\omega_\sigma)(\omega_{p0}-\omega_2)} \\ \gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) &= \hbar^{-3}\sum\mathscr{P}_{-\sigma,1,2,3} \\ &\times\left[\sum_{nmp}{}'\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\bar{\mu}}_\beta|m\rangle\langle m|\hat{\bar{\mu}}_\gamma|p\rangle\langle p|\hat{\mu}_\delta|0\rangle}{(\omega_{n0}-\omega_\sigma)(\omega_{m0}-\omega_2-\omega_3)(\omega_{p0}-\omega_3)}\right. \\ &\left.-\sum_{nm}{}'\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\bar{\mu}}_\beta|0\rangle\langle 0|\hat{\bar{\mu}}_\gamma|m\rangle\langle m|\hat{\mu}_\delta|0\rangle}{(\omega_{n0}-\omega_\sigma)(\omega_{m0}-\omega_3)(\omega_{m0}+\omega_2)}\right]\end{aligned}$$

$\sum\mathscr{P}_{-\sigma,1,2}$ denotes sum of six terms obtained by permuting pairs (α,ω_σ), (β,ω_1) and (γ,ω_2),while $\sum\mathscr{P}_{-\sigma,1,2,3}$ imples the sum of 24 terms with additional pair (δ,ω_3). $\bar{\hat{\mu}} = \hat{\mu} - \langle 0|\hat{\mu}|0\rangle$ is the fluctuation dipole moment operator. 5.399

8.6 Clamped nuclei approximation

Born–Oppenheimer approximation
The total molecular wavefunction is given as a product of electronic and nuclear terms:

$$|K,k\rangle = \phi_K^{el}(\mathbf{r},\mathbf{R}) \times \Psi_{K,k}^{nuc}(\mathbf{R})$$

$$\hat{H}^{el}(\mathbf{r},\mathbf{R})\phi_K^{el}(\mathbf{r},\mathbf{R}) = V_K^{el}(\mathbf{R})\phi_K^{el}(\mathbf{r},\mathbf{R})$$
$$\hat{H}_K^{nuc}(\mathbf{R})\Psi_{K,k}^{nuc}(\mathbf{R}) = \varepsilon_{K,k}^{nuc}\Psi_{K,k}^{nuc}(\mathbf{R})$$

Electrons create an effective potential for the nuclei, and for a given electronic state K whose energy depends parametrically on the nuclear configuration $\mathbf{R}$ and defines PES (k counts the vibrational states for a given electronic state K).

where:[20] 5.400

$$\hat{H}^{el}(\mathbf{r},\mathbf{R}) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \frac{e^2}{4\pi\varepsilon_0}\sum_{i\mu}\frac{Z_\mu}{r_{i\mu}} + \frac{e^2}{4\pi\varepsilon_0}\sum_{i>j}\frac{1}{r_{ij}}$$

$$\hat{H}_K^{nuc}(\mathbf{R}) = -\sum_{\mu=1}^{N}\frac{\hbar^2}{2M_\mu}\nabla_\mu^2 + \frac{e^2}{4\pi\varepsilon_0}\sum_{\mu>\nu}\frac{Z_\mu Z_\nu}{R_{\mu\nu}} + V_K^{el}(\mathbf{R})$$

5.401

Considering the product form of the total wavefunction and neglecting rovibrational couplings one my rewrite the derived expressions for (hyper)polarizabilities:

$$\alpha_{\alpha\beta}(-\omega;\omega) = \hbar^{-1}{\sum_{K,k}}' \left[\frac{\langle 0,0|\hat{\mu}_\alpha|K,k\rangle\langle k,K|\hat{\mu}_\beta|0,0\rangle}{\omega_{K,k}-\omega} + \frac{\langle 0,0|\hat{\mu}_\beta|K,k\rangle\langle k,K|\hat{\mu}_\alpha|0,0\rangle}{\omega_{K,k}+\omega}\right]$$

5.402

Since the electronic transition frequencies are usually much larger than vibrational ones and $\omega_{K,k} \approx \omega_{K0}$ one may partition these properties into electronic and vibrational contributions:

$$\alpha_{\alpha\beta}(-\omega;\omega) =$$
$$\hbar^{-1}{\sum_K}'\langle 0|\left[\frac{\langle 0|\hat{\mu}_\alpha|K\rangle\langle K|\hat{\mu}_\beta|0\rangle}{\omega_{K0}-\omega} + \frac{\langle 0|\hat{\mu}_\beta|K\rangle\langle K|\hat{\mu}_\alpha|0\rangle}{\omega_{K0}+\omega}\right]|0\rangle$$
$$+\hbar^{-1}{\sum_k}'\left[\frac{\langle 0|\mu_\alpha^{00}|k\rangle\langle k|\mu_\beta^{00}|0\rangle}{\omega_{k0}-\omega} + \frac{\langle 0|\mu_\beta^{00}|k\rangle\langle k|\mu_\alpha^{00}|0\rangle}{\omega_{k0}+\omega}\right]$$

where the summation in the first two terms runs over *electronic states* involving only the *ground vibrational state* $|K,0\rangle$ and in the latter two over *vibrational states* involving the *ground electronic state* $|0,k\rangle$, and $\mu^{00} = \langle 0|\hat{\mu}|0\rangle$. 5.403

[20] Please note that the nuclear repulsion is included in $\hat{H}_K^{nuc}(\mathbf{R})$

8.7 Vibrational contributions

The first two terms in the previous equation represent the electronic contribution averaged over the ground vibrational state and it is customary to partition these into *purely electronic* P^e and *zero-point vibrational averaging* P^{ZPVA} terms. The last two terms constitute the *purely vibrational* contribution P^v:

$$\begin{aligned} P &= P^e + P^{ZPVA} + P^v \\ P^{ZPVA} &= \langle 0|P^e(\mathbf{R})|0\rangle - P^e(\mathbf{R}_e) \end{aligned}$$

5.404

Bishop–Kirtman sum-over-states (SOS) perturbation theory (PT)

The pure vibrational contribution may be conveniently expressed in the so-called square-bracket notation:

$$\begin{aligned} \alpha^v(-\omega_\sigma;\omega_1) &= [\mu^2]^{0,0} + [\mu^2]^{2,0} + [\mu^2]^{1,1} \\ \beta^v(-\omega_\sigma;\omega_1,\omega_2) &= [\mu\alpha]^{0,0} + [\mu\alpha]^{2,0} + [\mu\alpha]^{1,1} \\ &\quad + [\mu^3]^{1,0} + [\mu^3]^{0,1} \\ \gamma^v(-\omega_\sigma;\omega_1,\omega_2,\omega_3) &= [\alpha^2]^{0,0} + [\alpha^2]^{2,0} + [\alpha^2]^{1,1} \\ &\quad + [\mu\beta]^{0,0} + [\mu\beta]^{2,0} + [\mu\beta]^{1,1} \\ &\quad + [\mu^2\alpha]^{1,0} + [\mu^2\alpha]^{0,1} + [\mu^4]^{2,0} + [\mu^4]^{1,1} \end{aligned}$$

The individual terms $[]^{n,m}$, where n and m denote the order of electrical and mechanical anharmonicity, respectively, may be computed from energy, dipole moment and (hyper)polarizability derivatives.

5.405

Double harmonic approximation

$$\begin{aligned} \alpha^v(-\omega_\sigma;\omega_1) &= [\mu^2]^{0,0} \\ \beta^v(-\omega_\sigma;\omega_1,\omega_2) &= [\mu\alpha]^{0,0} \\ \gamma^v(-\omega_\sigma;\omega_1,\omega_2,\omega_3) &= [\alpha^2]^{0,0} + [\mu\beta]^{0,0} \end{aligned}$$

5.406

Towards working formulae for the square bracket terms

In order to evaluate the matrix elements the dipolar polarization and vibrational potential are expanded in a power series in the normal coordinates Q_a:

$$\begin{aligned} \mu_\alpha &= \mu_\alpha^0 + \sum_a \frac{\partial \mu_\alpha}{\partial Q_a} Q_a + \frac{1}{2}\sum_a\sum_b \frac{\partial^2 \mu_\alpha}{\partial Q_a \partial Q_b} Q_a Q_b + \ldots \\ V &= V^0 + \frac{1}{2}\sum_a \omega_a^2 Q_a^2 + \frac{1}{6}\sum_a\sum_b\sum_c F_{abc} Q_a Q_b Q_c + \ldots \end{aligned}$$

5.407

Working formulae for lowest-order terms

$$
\begin{aligned}
[\mu^2] &= \sum_a \frac{(\frac{\partial \mu_\alpha^{el}}{\partial Q_a})_{Q_a=0}(\frac{\partial \mu_\beta^{el}}{\partial Q_a})_{Q_a=0}}{\omega_a^2} \\
[\mu\alpha] &= \frac{1}{2}\sum P_{-\sigma,1,2}\sum_a \frac{(\frac{\partial \mu_\alpha^{el}}{\partial Q_a})_{Q_a=0}(\frac{\partial \alpha_{\beta\gamma}^{el}}{\partial Q_a})_{Q_a=0}}{\omega_a^2} \\
[\alpha^2] &= \frac{1}{8}\sum P_{-\sigma,1,2,3}\sum_a \frac{(\frac{\partial \alpha_{\alpha\beta}^{el}}{\partial Q_a})_{Q_a=0}(\frac{\partial \alpha_{\gamma\delta}^{el}}{\partial Q_a})_{Q_a=0}}{\omega_a^2} \\
[\mu\beta] &= \frac{1}{6}\sum P_{-\sigma,1,2,3}\sum_a \frac{(\frac{\partial \mu_\alpha^{el}}{\partial Q_a})_{Q_a=0}(\frac{\partial \beta_{\beta\gamma\delta}^{el}}{\partial Q_a})_{Q_a=0}}{\omega_a^2}
\end{aligned}
$$

5.408

8.8 Computational approaches for estimation of molecular (hyper)polarizabilities

Time-independent external perturbation

In the limit of static fields the relaxed wavefunction is stationary and the field-dependent energy $E(\mathbf{F})$ may be determined as the expectation value of the Hamiltonian:

$$\hat{H}|\psi(\mathbf{F})\rangle = E(\mathbf{F})|\psi(\mathbf{F})\rangle$$

where

$$\hat{H} = \hat{H}_0 - \hat{\mu}_\alpha F_\alpha$$

Considering derivative of the energy with respect to the external electric field:

$$
\begin{aligned}
\frac{\partial E(\mathbf{F})}{\partial F_\alpha} = \frac{\partial}{\partial F_\alpha}\langle\psi(\mathbf{F})|\hat{H}|\psi(\mathbf{F})\rangle &= \left\langle \frac{\partial \psi(\mathbf{F})}{\partial F_\alpha}|\hat{H}|\psi(\mathbf{F})\right\rangle \\
&+ \left\langle \psi(\mathbf{F})|\hat{H}|\frac{\partial \psi(\mathbf{F})}{\partial F_\alpha}\right\rangle + \left\langle \psi(\mathbf{F})|\frac{\partial \hat{H}}{\partial F_\alpha}|\psi(\mathbf{F})\right\rangle
\end{aligned}
$$

5.409

Since any variational wave function is optimal for any variation and $\delta\langle\psi|\hat{h}|\psi\rangle = 0$ the derivative simplifies by virtue of Hellmann–Feynmann theorem to:

$$
\begin{aligned}
\frac{\partial E(\mathbf{F})}{\partial F_\alpha} &= \left\langle \psi(\mathbf{F})|\frac{\partial \hat{H}}{\partial F_\alpha}|\psi(\mathbf{F})\right\rangle \\
\frac{\partial E(\mathbf{F})}{\partial F_\alpha} &= -\langle\psi(\mathbf{F})|\hat{\mu}|\psi(\mathbf{F})\rangle = -\mu_\alpha(\mathbf{F})
\end{aligned}
$$

thus to retrieve the permanent dipole moment:

$$\mu_\alpha^0 = -\left.\frac{\partial E(\mathbf{F})}{\partial F_\alpha}\right|_{F=0}$$

The above equation implies that one may alternatively use energy expansion instead of dipole moment expansion.

5.410

Two alternative Taylor series expansions ...

$$
\begin{aligned}
E(\mathbf{F}) &= E(0) - \mu_\alpha F_\alpha - \frac{1}{2!}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{3!}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma \\
&\quad - \frac{1}{4!}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta - \dots \\
\mu_\alpha(\mathbf{F}) &= \mu^0_\alpha + \alpha_{\alpha\beta}F_\beta + \frac{1}{2!}\beta_{\alpha\beta\gamma}F_\beta F_\gamma \\
&\quad + \frac{1}{3!}\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta + \dots
\end{aligned}
$$

5.411

... and the corresponding formulas for static (hyper)polarizabilities

$$
\begin{aligned}
\mu^0_\alpha &= -\left.\frac{\partial E(\mathbf{F})}{\partial F_\alpha}\right|_{F=0} \\
\alpha_{\alpha\beta} &= -\left.\frac{\partial^2 E(\mathbf{F})}{\partial F_\alpha \partial F_\beta}\right|_{F=0} &&= \left.\frac{\partial \mu_\alpha(\mathbf{F})}{\partial F_\beta}\right|_{F=0} \\
\beta_{\alpha\beta\gamma} &= -\left.\frac{\partial^3 E(\mathbf{F})}{\partial F_\alpha \partial F_\beta \partial F_\gamma}\right|_{F=0} &&= \left.\frac{\partial^2 \mu_\alpha(\mathbf{F})}{\partial F_\beta \partial F_\gamma}\right|_{F=0} \\
\gamma_{\alpha\beta\gamma\delta} &= -\left.\frac{\partial^4 E(\mathbf{F})}{\partial F_\alpha \partial F_\beta \partial F_\gamma \partial F_\delta}\right|_{F=0} &&= \left.\frac{\partial^3 \mu_\alpha(\mathbf{F})}{\partial F_\beta \partial F_\gamma \partial F_\delta}\right|_{F=0}
\end{aligned}
$$

5.412

Finite-Field method

The most straightforward method[21] to calculate the required derivatives is to truncate the energy or dipole moment expansion and solve for the desired coefficients by numerical differentiation using central-differences[22] method by feeding in the energies calculated on an N-point regular grid around a central field $F^* = 0$:

$$
F_z^k = F^* + kh,\ k = -\frac{N-1}{2}, \dots, \frac{N-1}{2}
$$

where h is a small field step (usually about 0.001 a.u.).
To calculate the required energies of a molecule in a uniform field $\mathbf{F}$ one needs only to modify one-electron integrals:

$$
h_{ij}(\mathbf{F}) = \langle \phi_i | \hat{h} | \phi_j \rangle - e\langle \phi_i | \hat{\mu}_\alpha | \phi_j \rangle F_\alpha
$$

5.413

For instance, if we truncate the energy expansion after quadratic term and focus on components along z-axis,

$$
E(F_z) = E(0) - \mu_z F_z - \frac{1}{2}\alpha_{zz}F_z^2
$$

[21] Roothaan, Cohen, Bartlett, Purvis, Kurtz
[22] http://www.holoborodko.com

we can solve this for μ_z and α_{zz} if we calculate $E(-F_z)$, $E(0)$ and $E(+F_z)$:

$$\mu_z = \frac{E(-F_z) - E(F_z)}{2F_z}$$
$$\alpha_{zz} = \frac{2E(0) - (E(F_z) + E(-F_z))}{F_z^2}$$

5.414

In general, we are left with a set of linear equations, which for diagonal terms using 5-point stencil central-difference can be put as follows:

$$\begin{pmatrix} -F_i & -\frac{1}{2}F_i^2 & -\frac{1}{6}F_i^3 & -\frac{1}{24}F_i^4 \\ F_i & -\frac{1}{2}F_i^2 & \frac{1}{6}F_i^3 & -\frac{1}{24}F_i^4 \\ -2F_i & -\frac{1}{2}(2F_i)^2 & -\frac{1}{6}(2F_i)^3 & -\frac{1}{24}(2F_i)^4 \\ 2F_i & -\frac{1}{2}(2F_i)^2 & \frac{1}{6}(2F_i)^3 & -\frac{1}{24}(2F_i)^4 \end{pmatrix} \cdot \begin{pmatrix} \mu_i \\ \alpha_{ii} \\ \beta_{iii} \\ \gamma_{iiii} \end{pmatrix} = \begin{pmatrix} E(F_i) - E(0) \\ E(-F_i) - E(0) \\ E(2F_i) - E(0) \\ E(-2F_i) - E(0) \end{pmatrix}$$

5.415

5-point stencil formulas for the diagonal terms

$$\alpha_{zz}|F_z|^2 = \frac{5}{2}E(0) - \frac{4}{3}[E(F_z) + E(-F_z)] + \frac{1}{12}[E(2F_z) + E(-2F_z)]$$
$$\alpha_{zz}|F_z| = \frac{2}{3}[\mu_z(F_z) - \mu_z(-F_z)] - \frac{1}{12}[\mu_z(2F_z) - \mu_z(-2F_z)]$$
$$\beta_{zzz}|F_z|^3 = [E(F_z) - E(-F_z)] - \frac{1}{2}[E(2F_z) - E(-2F_z)]$$
$$\beta_{zzz}|F_z|^2 = \frac{1}{3}[\mu_z(2F_z) + \mu_z(-2F_z) - \mu_z(F_z) - \mu_z(-F_z)]$$
$$\gamma_{zzzz}|F_z|^4 = -6E(0) + 4[E(F_z) + E(-F_z)] - [E(2F_z) + E(-2F_z)]$$
$$\gamma_{zzzz}|F_z|^3 = \frac{1}{2}[\mu_z(2F_z) - \mu_z(-2F_z)] - [\mu_z(F_z) - \mu_z(-F_z)]$$

5.416

Romberg–Rutishauser algorithm

At the heart of RR scheme is the following stencil at which we need to evaluate the values of chosen functions (e.g. E or μ):

$$(-2^k h, -2^{k-1}h, -2^{k-2}h, \ldots, -2h, -h, 0, h, 2h, \ldots, 2^{k-2}h, 2^{k-1}h, 2^k h)$$

where h is the nominal step size and k is the order of RR iteration. Then, for a given k^{th} point the central difference approximation for n^{th} derivative of a function $f(x)$ ($f^{(n)}(x)$) can be calculated:

$$
\begin{aligned}
f^{(1)}(x) \approx \delta^{(1),k} &= \frac{f(2^k h) - f(-2^k h)}{2^{k+1} h} \\
f^{(2)}(x) \approx \delta^{(2),k} &= \frac{f(-2^k h) + f(2^k h) - 2f(0)}{(2^k h)^2} \\
f^{(3)}(x) \approx \delta^{(3),k} &= \frac{-f(-2^{k+1} h) + 2f(-2^k h) - 2f(2^k h) + f(2^{k+1} h)}{2(2^k h)^3} \\
f^{(4)}(x) \approx \delta^{(4),k} &= \frac{f(-2^{k+1} h) - 4f(-2^k h) + 6f(0) - 4f(2^k h) + f(2^{k+1} h)}{(2^k h)^4}
\end{aligned}
$$

5.417

Unfortunately, the zeroth-order terms suffer from higher-order differentiation contaminations. These, however, can be removed in the following iterative scheme:

$$
D^{n,k} = \frac{4^n \cdot D^{n-1,k} - D^{n-1,k-1}}{4^n - 1}
$$

where D is the required-order derivative, n counts the RR iterations, and $D^{0,k}$ are the zeroth-order derivatives of at k^{th} point.[23]

5.418

Generalized Romberg–Rutishauser algorithm

Recently Medved' et al. proposed an improved scheme in which the quotient between the grid points can be chosen arbitrarily (in RR it equals 2) what allows for a denser stencil and larger field steps.

$$
D^{(n,k)} = \frac{a^{2n} D^{(n-1,k)} - D^{(n-1,k+1)}}{a^{2n} - 1}
$$

where D is the required-order derivative, a is the quotient (for instance $\sqrt{2}$) n counts the GRR iterations, and $D^{0,k}$ are the zeroth-order derivatives of at k^{th} point.[23]

5.419

[23] Please check http://wiki.zcht.info for our in-house python application *ff.py* which does this and a lot more.

References

[1] P. W. Atkins and R. Friedman, *Molecular quantum mechanics*, 5th ed. Oxford ; New York: Oxford University Press, 2011.

[2] T. Engel and P. Reid, *Quantum Chemistry and Spectroscopy*, 3rd ed. Boston: Pearson, 2013.

[3] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems*, 3rd. Wiley-VCH Verlag GmbH & Co. KGaA, 2011.

[4] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, Courier Corporation, 2012.