CHM4M3 : Quantum Mechanics (for chemistry students)

K. Ando
School of Chemistry, University of Birmingham

http://www.chem.bham.ac.uk/labs/ando/chm4m3.pdf

Last updated : December 1, 2004

Contents

1 Quantum Effects in Chemistry .................................................. 4
  1.1 Discrete energy levels ....................................................... 4
  1.1.1 Coulomb potential ..................................................... 4
  1.1.2 Box potential .......................................................... 5
  1.1.3 Harmonic oscillator .................................................... 5
  1.2 Zero-point motion .......................................................... 6
  1.3 Tunneling .......................................................................... 6
  1.4 Resonance and interference ............................................... 7

2 Schrödinger Equation ............................................................... 7
  2.1 Time-dependent Schrödinger equation ................................. 8
  2.2 Stationary state ............................................................... 9

3 Simple systems ........................................................................ 10
  3.1 1-dimensional free particle ................................................ 10
  3.2 Wave packet ...................................................................... 11
  3.3 Box potential ..................................................................... 13
  3.4 Classically forbidden regions ............................................. 14

4 Perturbation and Variation Methods ......................................... 15
  4.1 Helium atom ..................................................................... 15
  4.2 Perturbation Theory (time-independent) ............................ 16
  4.3 Variational method .......................................................... 18
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>Summary: Perturbation Theory (time-independent)</td>
<td>19</td>
</tr>
<tr>
<td>4.5</td>
<td>Summary: Variational Theorem</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>LCAO-MO Method</td>
<td>22</td>
</tr>
<tr>
<td>5.1</td>
<td>Diatomic molecule</td>
<td>22</td>
</tr>
<tr>
<td>5.2</td>
<td>Generalization</td>
<td>25</td>
</tr>
<tr>
<td>5.3</td>
<td>Hückel MO theory</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>Variation-perturbation method</td>
<td>26</td>
</tr>
<tr>
<td>6.1</td>
<td>Application: Charge-transfer complex</td>
<td>28</td>
</tr>
<tr>
<td>6.1.1</td>
<td>Intermolecular CT spectra</td>
<td>28</td>
</tr>
<tr>
<td>6.2</td>
<td>Application: Frontier MO theory</td>
<td>29</td>
</tr>
<tr>
<td>7</td>
<td>Electronic polarizability</td>
<td>31</td>
</tr>
<tr>
<td>7.1</td>
<td>Quantum mechanical expression</td>
<td>31</td>
</tr>
<tr>
<td>7.2</td>
<td>Closure approximation</td>
<td>33</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Preparation</td>
<td>33</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Hermite operator</td>
<td>34</td>
</tr>
<tr>
<td>7.2.3</td>
<td>Closure approximation</td>
<td>34</td>
</tr>
<tr>
<td>7.2.4</td>
<td>Approximation of polarizability</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>Time-dependent perturbation theory</td>
<td>36</td>
</tr>
<tr>
<td>8.1</td>
<td>Time-dependent interaction</td>
<td>36</td>
</tr>
<tr>
<td>8.2</td>
<td>Two-states resonance</td>
<td>37</td>
</tr>
<tr>
<td>8.3</td>
<td>Perturbation theory</td>
<td>38</td>
</tr>
<tr>
<td>8.4</td>
<td>Fermi’s golden rule</td>
<td>39</td>
</tr>
<tr>
<td>8.5</td>
<td>First-order spectra</td>
<td>40</td>
</tr>
<tr>
<td>8.6</td>
<td>Franck-Condon principle</td>
<td>40</td>
</tr>
<tr>
<td>Appendices</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>A</td>
<td>Gaussian wave packet</td>
<td>42</td>
</tr>
<tr>
<td>B</td>
<td>Effective Hamiltonian</td>
<td>43</td>
</tr>
<tr>
<td>C</td>
<td>Frontier MO Theory</td>
<td>44</td>
</tr>
<tr>
<td>D</td>
<td>Energy change under electric field</td>
<td>45</td>
</tr>
</tbody>
</table>
Readings

   *Basic. Essential for chemistry undergraduates.*

2. Atkins and Friedman, Molecular Quantum Mechanics, Oxford. (£35)
   *Advanced. Includes modern topics. Good reference for both postgraduates and researchers.*

3. Pauling and Wilson, Introduction to Quantum Mechanics: With Applications to Chemistry, Dover. (£7)
   *Advanced classic. Maths derivations are more detailed than Atkins-Friedman.*

   *Classic. Chapter 3 is a compact summary of quantum mechanics for chemists.*
Quantum effects are typically observed in chemical problems such as

- discrete energy levels (electronic states, vibration, rotation)
- zero-point motion (molecular vibrations, phonons in solids)
- tunneling (electrons, light atoms such as H, He)
- resonance and interference

Note that these phenomena cannot be understood in terms of Classical Mechanics which can nonetheless describe the motion of macroscopic objects very well. In this introductory section, we survey the **qualitative** aspects of these quantum phenomena.

### 1.1 Discrete energy levels

#### 1.1.1 Coulomb potential

In the hydrogen-like (i.e., one-electron) atoms, the electron is subject to the Coulomb potential from the nucleus:

\[ V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \]  

where \( Ze \) is the nuclear charge and \( r \) is the distance between the electron and the nucleus. The electronic energy levels are given by

\[ E_n = -\frac{\mu^2 Z^2}{32\pi^2\epsilon_0^2\hbar^2 n^2} = -\frac{\hbar c R_H Z^2}{n^2} \propto -\frac{1}{n^2} \]  

where \( R_H \) = Rydberg constant, \( \mu = \) reduced mass \( \simeq m_e \).

- Note that the energy spacing \( \Delta E \) **decreases** as we go up the energy levels (or the quantum number \( n \)).
1.1.2 Box potential

\[ V(x) = \begin{cases} 
0 & (0 < x < L) \\
+\infty & (x \leq 0, \quad x \geq L) 
\end{cases} \quad (1.3) \]

\[ \psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \quad (1.4) \]

\[ E_n = \frac{n^2\hbar^2}{8mL^2} \propto n^2 \quad (1.5) \]

- \( \Delta E \) increases as the energy (or \( n \)) goes up.

**Question:** Delete as appropriate.

1. \( \Delta E \) increases/decreases as the mass of the particle \( m \) increases.

2. \( \Delta E \) increases/decreases as the size of the box \( L \) increases.

- The quantum effect is large for light particles (e.g. e\(^-\), H, He) confined in a small region.

1.1.3 Harmonic oscillator

\[ V(x) = \frac{1}{2}kx^2 \quad (k = \text{force constant}) \quad (1.6) \]

\[ E_n = (n + \frac{1}{2})\hbar\omega, \quad \omega = \sqrt{\frac{k}{m}} \quad \text{(frequency)} \quad (1.7) \]

\[ \Delta E_n = E_{n+1} - E_n = \hbar\omega \quad \text{(independent of} \ n) \quad (1.8) \]
Questions

1. How would you interpret qualitatively the different behavior of $\Delta E$ among the three (Coulomb, Box, Harmonic) potentials?

2. Draw schematically a potential energy curve for a diatomic molecule and the vibrational energy levels. How would you interpret the behavior of $\Delta E$?

3. Add a schematic drawing of an excited electronic state potential curve. How would you interpret the fact that the electronic excitation energies are generally much larger than the vibrational excitation energies?

4. Do you think that we can detect quantized energy levels of the translational motions of molecules? Why / In what condition?

5. In an ideal situation where the translational motion of a quantum particle is ‘free’, i.e., no confinement by a potential, it can take any energy. In other words, it has a continuous energy level. Now, why do you think is the ‘free’ rotation of a molecule quantized, i.e., has discrete energy levels? What is the difference from the free translation?

1.2 Zero-point motion

Question: Describe and compare in classical and quantum mechanics the lowest energy state of a particle in a bound potential. Does the particle have kinetic energy? How does the probability of finding the particle depend on the position?

1.3 Tunneling

Quantum tunneling: classically forbidden transmission through a potential barrier. In chemistry,

- Long-distance electron transfer (redox) reactions
- Proton / hydrogen / hydride transfers and migrations
- Excitation energy transfers (photochemistry)
- Electronic devices (tunneling diode etc.)
- Super-fluid state of liquid He / chemistry in liquid He
1.4 Resonance and interference

Even when the energy of a quantum mechanical particle is above the potential maximum, there is a finite probability of reflection. In this case, the transmission probability oscillates as a function of energy. This is called “anti-tunneling” or “non-classical reflection”. These phenomena comes from the resonance behavior of the wavefunction. In chemistry, this is observed in e.g. gas-phase molecular beam scattering experiments. It is also considered that the resonance of electron motion is relevant in the long-distance electron transfer (redox) reactions in biomolecules.

2 Schrödinger Equation

In classical mechanics, the dynamics of a particle is completely specified by its trajectory, i.e., the evolution of the position \( x(t) \) and momentum \( p(t) \) along time \( t \). Given the starting position and momentum at a certain time, the trajectory in the future is predicted by Newton’s equation. In principle, we are able to observe the (classical) trajectory by detecting the reflected light from the particle.

The situation is radically different for quantum mechanical particles such as atoms and electrons. Precise determination of their trajectories is much less plausible since, firstly, we don’t have the resolution shorter than the wavelength of the probe light. The wavelength of visible light is in the range of 400-700 nm, which is far longer than the dimension of atoms. If we use a shorter wavelength to obtain higher resolution, then the photon energy becomes larger and the tiny quantum particle are easily scattered off by the probe photon. This imposes a fundamental difficulty on the simultaneous observation of the position and momentum of quantum particles. *

*To measure the momentum of a quantum particle, e.g. an electron, we observe the Compton
This imprecision in the simultaneous determination of position and momentum is postulated to be a fundamental law of quantum physics, which is called “Heisenberg’s uncertainty principle”. It also implies that the quantum mechanical equation of motion will not have a form to predict in a direct way the particle trajectory \((x(t), p(t))\) itself.

It turned out during the first 30 years of the last century that we need to introduce an auxiliary substance called wave function, which is assumed to represent the quantum mechanical state of the system. Instead of getting directly to the trajectory, we have to look at the wave function in order to find the possible set of numbers that may result from the measurements of \(x(t)\) and \(p(t)\), and various other physical quantities.

Then, what actually is this mysterious auxiliary quantity? Is it something real, or just a mathematical accessory in order to help our calculations of the physical quantities? When we start asking these kind of questions, we might fall into the ‘philosophical’ problems such as ‘what do we mean by a real substance, or the reality per se?’ etc. Indeed, there are lots of issues to discuss around the conceptual foundation of quantum mechanics, on which we still do not seem to have achieved completely agreed understanding. These are considered to be important for clarifying the problem of reconciling the classical mechanical world of our ordinary life and the quantum mechanical world of the microscopic constituents. And furthermore, this problem may be related to a purely technical issue of simulating chemical reactions, where the heavy nuclei might be treated by classical mechanics and the electrons by quantum mechanics. In this lecture course, however, we do not venture to dive into these kind of problems but rather try to see (and get accustomed to) how it actually works in some well-established chemical problems.

### 2.1 Time-dependent Schrödinger equation

The wave function \(\Psi(x, t)\) evolves along time according to

\[
i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \hat{H}\Psi(x, t)
\]  

(2.1)

For a particle (mass \(m\)) in a potential, the Hamiltonian is given by

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x)
\]  

(2.2)

recoil of the photon scattering, which is subject to uncertainties limited by the directional resolution of the microscope.
where $\nabla$ is an operator to give the gradient vector of a scalar function, i.e., $\nabla f = (\partial f/\partial x, \partial f/\partial y, \partial f/\partial z)$. Its square $\nabla^2$, called Laplacian operator, is defined by

$$\nabla^2 \Psi(x) = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}$$ (2.3)

The first term in $\hat{H}$ represents the kinetic energy of the particle $p^2/2m$, after applying the quantum correspondence of the momentum $p = -i\hbar \nabla$. The second derivative $\nabla^2 \Psi$ represents the curvature of the wave function, so the oscillatory behavior in space (or the ‘wave number’ as will be discussed later) determines the kinetic energy of the particle.

### 2.2 Stationary state

We assume here that the solution of the time-independent Schrödinger equation

$$\hat{H} \psi(x) = E \psi(x)$$ (2.4)

is known. Then, what does this mean for the time evolution of the system according to the time-dependent Schrödinger equation (2.1)?

When we have the solution of Eq (2.4), the time-dependent wave function $\Psi(x,t)$ is factorized into a product of time and space parts such as $\Psi(x,t) = f(t)\psi(x)$, so that Eq (2.1) simplifies as

$$i\hbar \frac{df}{dt} \psi(x) = f(t)\hat{H} \psi(x) = f(t)E \psi(x)$$ (2.5)

Therefore, the time-dependent part $f(t)$ satisfies a simple 1st-order differential equation

$$i\hbar \frac{df}{dt} = Ef(t)$$ (2.6)

whose solution is

$$f(t) = C e^{-iEt/\hbar} = C[\cos(Et/\hbar) - i \sin(Et/\hbar)]$$ (2.7)

The arbitrary constant $C$ is not important for the current discussion (it is determined from the normalization of the wave function), so we simply put $C = 1$. The time-dependent wave function is then expressed as

$$\Psi(x,t) = \psi(x) e^{-iEt/\hbar}$$ (2.8)

This means that $\Psi(x,t)$ is a **standing wave** oscillating at frequency $E/\hbar$. 


Notes:

1. In many textbooks, the time-independent equation (2.4) is derived from the time-dependent Schrödinger equation (2.1) via separation of variables. On the other hand, we have taken here an easier route by assuming that the total wave function can be factorized into the time and space part. It would be useful to read and compare these different treatments.

2. We need some additional care when the Hamiltonian explicitly depends on time. This will be treated in Sec 8 dealing with the time-dependent perturbation theory with applications to molecular spectroscopy.

3 Simple systems

In this chapter, we discuss a few of the simplest systems; a free particle, a particle in a box, and a particle in a rectangular potential well or colliding to a rectangular potential wall. The wave packet picture, which reconciles the mysterious duality of quantum particles, i.e., the wave and particle duality, is also introduced. All these are aimed to develop good qualitative pictures of quantum systems which may carry over to other problems.

3.1 1-dimensional free particle

Free particle ... \( V(x) = 0 \),

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \] (3.1)

The time-independent Schrödinger equation

\[ -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E \psi(x) \] (3.2)

whose general solution has a form

\[ \psi(x) = A \, e^{ikx} + B \, e^{-ikx} \] (3.3)

where \( A \) and \( B \) are at this stage arbitrary constants. They represent the amplitude of the wave function. \( k \) is called wave number, the number of waves per unit length \( (\times 2\pi) \), i.e., \( k = 2\pi/\lambda \) where \( \lambda \) is the wave length.
**Question:**

1. Confirm that Eq (3.3) satisfies Eq (3.2), and express the energy $E$ in terms of $k$ and other physical parameters.

2. Does the energy $E$ exhibit discrete levels or a continuum? In other words, is there any condition that limits the value of $k$ in order for $\psi(x)$ to satisfy Eq (3.2)? (This is to be compared with Question 2 of Sec 3.3.) What is its physical implication? Is there any connection to Sec 1.1?

From Sec 2.2, the time-dependent wave function is expressed as

$$\psi(x)e^{-iEt/\hbar} = A e^{i(kx-Et/\hbar)} + B e^{-i(kx+Et/\hbar)} = A e^{ik(x-\hbar/k^2mt)} + B e^{-ik(x+\hbar/k^2mt)} \equiv A \psi_k(x,t) + B \psi_{-k}(x,t)$$

(3.4)

The last line defines $\psi_k(x,t)$. We find from the exponents $x \pm \hbar/k^2mt$ that the first/second term represents a traveling wave propagating toward the positive/negative direction of $x$ with a velocity $\frac{\hbar k}{2m}$. †

**Question:** Show that $\psi_k(x,t)$ is an eigenfunction of the momentum operator $\hat{p} = -i\hbar \frac{d}{dx}$.

### 3.2 Wave packet

The wave function derived above, although being mathematically correct solution for the free particle Hamiltonian, is not physically adequate because it is delocalized over the whole range of space $-\infty < x < +\infty$, and therefore the normalization integral diverges.

$$\int_{-\infty}^{+\infty} |\psi_k(x,t)|^2 dx = \int_{-\infty}^{+\infty} 1 dx = \infty$$

(3.5)

†This velocity $\hbar k/2m$ is the so-called phase velocity of the wave. On the other hand, as seen from the Question, $\psi_k(x,t)$ has a definite momentum of $\hbar k$, which implies that the velocity is $v = p/m = \hbar k/m$, being different from the phase velocity by a factor of 2. This ostensible paradox is resolved by considering a wave packet as in the next section and in Appendix A. To summarize, we find that it is the group velocity of the wave packet, i.e., the velocity of the embracing envelope of the packet, that corresponds to $\hbar k/m$, in accordance with the classical mechanical velocity derived from $E = mv^2/2 = \hbar^2 k^2/2m$. On the other hand, the phase velocity describes the motion of the ripples within the wave packet, which may be different from the group velocity of the envelope.
(In fact, this is related to the uncertainty principle. As we have seen in the Question above, the wave function $\psi_k(x, t)$ has a **definite** momentum $p = \hbar k$, which means that its position is completely uncertain.)

To remedy this divergence, we consider a superposition of $\psi_k$’s having a range of $k$’s, which will localize the wave function via “dephasing”. Namely, by mixing waves of slightly different wave length, we observe the cancellation, or the destructive interference, of the waves as we get away from the center (see the figure). Indeed, this recovers the particle picture of the free-‘particle’.

This superposition can be described by using some appropriate weight factors, $w_{k_i}$, for the $i$-th component of the wave number $k_i$ such as

\[
\psi_{wp}(x, t) = \sum_i w_{k_i} \psi_{k_i}(x, t) \tag{3.6}
\]

or by using a continuous weight function $w(k)$,

\[
\psi_{wp}(x, t) = \int w(k) \psi_k(x, t) dk \tag{3.7}
\]

An important example of Gaussian shape wave-packet is described in Appendix A.

While each component $\psi_k$ is an eigenfunction of (i.e. solution of) the time-independent Schrödinger equation (3.2), their superposition $\psi_{wp}$ is not, for it is a mixture of $\psi_k$’s having different energies $E_k = \hbar^2 k^2 / 2m$. Namely,

\[
\hat{H}\psi_{wp}(x, t) = \sum_i w_{k_i} \frac{\hbar^2 k_i^2}{2m} \psi_{k_i}(x, t) \quad \text{or} \quad \int w(k) \frac{\hbar^2 k^2}{2m} \psi_k(x, t) dk \tag{3.8}
\]

is not proportional to $\psi_{wp}(x, t)$. But this does not cause any trouble. If it were a solution of the time-independent Schrödinger equation, as we saw in Sec 2.2, it should represent a stationary standing wave and therefore does not fit with the picture of a flying free ‘particle’. In other words, being the solution of the time-independent
Schrödinger equation is not a requirement, but just the condition to be in a stationary state having a definite energy. The time-dependent Schrödinger equation (2.1) is a more general and fundamental law, by which the dynamics of the wave functions $\Psi(x, t)$ are predicted.

### 3.3 Box potential

Let us now revisit the 1-dimensional box potential considered briefly and qualitatively in Sec 1.1.2. We first note that the equation should be the same as the free particle case in the region $0 < x < L$, so the wave function in this region has the form

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$  \hspace{1cm} (3.9)

However, we now have a different condition from the free particle case such that the potential diverges to $+\infty$ at the boundaries $x = 0$ and $L$. Since it is physically unacceptable to allow the particle to have a probability to be found in the region of infinite potential energy, the wave function must vanish at these boundaries

$$\psi(0) = \psi(L) = 0$$  \hspace{1cm} (3.10)

These two conditions limit the possible values of $A$, $B$ and $k$. Before starting the maths, let us review the diagram in Sec 1.1.2 and see that in order for the wave function to fit within the length $L$ with the conditions Eq (3.10), the wave length $\lambda$ must satisfy

$$L = \frac{\lambda}{2} \times n \hspace{0.5cm} (n = 1, 2, 3, \cdots)$$  \hspace{1cm} (3.11)

**Question:**

1. From $\psi(0) = 0$, show that $\psi(x)$ is proportional to a sine function of $x$.

2. From $\psi(L) = 0$ show that $kL$ is limited to be $n\pi$ where $n$ is any integer number. Confirm that this corresponds to Eq (3.11).

3. Show that the solution with $n = 0$ is not physically acceptable.

4. Show that the sets of wave functions with negative and positive $n$ are not independent from each other. Therefore, an independent set of wave functions can be specified only by positive $n$.

5. Remember how we derived $E = \hbar^2 k^2 / 2m$ for the free particle. Does this also apply for the present case of the box potential? Using this and the condition for $k$ obtained in Question 2, derive Eq (1.5).
We have found $\psi(x) \propto \sin(n\pi x/L)$. In order to completely determine the wave function, we impose the normalization condition, $\int_0^L |\psi(x)|^2 dx = 1$, which finally gives Eq (1.4).

### 3.4 Classically forbidden regions

We now consider a rectangular barrier potential with height $V_0$,

$$V(x) = \begin{cases} V_0 & (0 < x < L) \\ 0 & (x \leq 0, \ x \geq L) \end{cases} \quad (3.12)$$

and assume that the energy of the incident particle $E$ is smaller than the barrier, $E < V_0$. Again, outside the barrier region, in $x \leq 0$ and $x \geq L$ where $V(x) = 0$, the wave function has the same form as the free-particle case

$$\psi(x) = A e^{ikx} + B e^{-ikx} \quad (3.13)$$

In the barrier region $0 < x < L$, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_0 \quad (3.14)$$

The Schrödinger equation is similar to the free-particle case, but now the energy is shifted by a constant $V_0$. Let us denote the wave function in this region as $\phi(x)$. The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} = (E - V_0) \phi(x) \quad (3.15)$$

Because $E - V_0 < 0$, the solution is qualitatively different from the free particle case – it is given by the ordinary (real) exponential functions

$$\phi(x) = A' e^{\kappa x} + B' e^{-\kappa x} \quad (3.16)$$

Note the difference from the oscillatory complex function $e^{\pm ikx}$ for the free-particle case. The functions $e^{\pm\kappa x}$ are monotonic. The difference stems from the sign of $E - V_0 < 0$.

The remaining task is to joint smoothly the oscillatory function $\psi(x)$ and the monotonic function $\phi(x)$ at the boundaries $x = 0$ and $L$. The condition is such that both the functions $\psi$ and $\phi$ and their gradients $d\psi/dx$ and $d\phi/dx$ are continuous at the boundaries.
The precise mathematical expression is rather involved even for this simple rectangular barrier case (see the textbooks for details), but the basic idea itself is as simple as described qualitatively here, which is sufficient to sketch the wave function schematically.

Question:

1. Draw schematically the wave functions in a rectangular well potential having a finite depth (as in the middle of the diagrams in Sec 1.4, but with the energy levels in the well).

2. Look at the wave functions of harmonic oscillator shown in Sec 1.1.3. Do they show qualitatively similar behavior?

4 Perturbation and Variation Methods

4.1 Helium atom

The Hamiltonian of a helium atom is, neglecting the motion of the nucleus, given by

\[ H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \]  

Here and hereafter we omit, just for notational simplicity, the constant factor $1/4\pi\epsilon_0$ from the Coulomb potential. Even for this simple two-electron atom, the Schrödinger equation

\[ H\psi(r_1, r_2) = E\psi(r_1, r_2) \]
has not been solved analytically. Indeed, we have only limited number of systems that have been solved analytically, e.g., free particle, rectangular potential, harmonic oscillator, and Coulomb potential (hydrogen-like atoms). In practice, as in classical mechanics, it is nearly hopeless to obtain analytical solutions when more than two particles are interacting. In chemical applications, therefore, we almost inevitably need to resort to variety of approximation techniques, of which two representatives are the perturbation and variation methods.

Both of these have time-independent and dependent versions. We illustrate and compare the time-independent ones by using the helium atom as an illustrative example. The time-dependent perturbation theory will be discussed in Sec 8 with applications to molecular spectroscopy. The time-dependent variation theory is a rather advanced topic and will not be treated in this lecture. ‡

### 4.2 Perturbation Theory (time-independent)

We divide the Hamiltonian into two parts

\[
H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze_1^2}{r_1} - \frac{Ze_2^2}{r_2} + \frac{e^2}{r_{12}}
\]

\[
= H_0 + H'
\]

Note that \(H_0\) is a sum of the hydrogen-like § Hamiltonians for each of the two electrons

\[
H_0 = h_0(r_1) + h_0(r_2)
\]

\[
h_0(r) = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r}
\]

for which we already know that the exact analytical solutions are the s, p, d, \(\cdots\) atomic orbitals (e.g. Eq (4.10) below). For example, the 1s function \(\chi_{1s}(r)\) satisfies

\[
h_0(r)\chi_{1s}(r) = E_{1s}\chi_{1s}(r)
\]

where \(E_{1s}\) denotes the 1s energy level (see Question 3 below).

Now suppose that we neglected the electron-electron interaction \(H'\) and only consider the two electron system with \(H_0\). Without the interaction \(H'\), the motions of

---


§The hydrogen-like atoms are one-electron atoms such as H, He\(^+\), Li\(^{2+}\), Be\(^{3+}\), \(\cdots\).
the two electrons are independent of each other. Therefore, they each follow their own H-like Hamiltonian \( h_0 \) such that to occupy the 1s orbital independently. The solution of the Schrödinger equation

\[
H_0 \psi^{(0)}(r_1, r_2) = E^{(0)} \psi^{(0)}(r_1, r_2),
\]

is thus given by a simple product of \( \chi_{1s} \)’s of each electron

\[
\psi^{(0)}(r_1, r_2) = \chi_{1s}(r_1)\chi_{1s}(r_2)
\]

Note that this looks in accordance with the Aufbau configuration, He : (1s)\(^2\)

**Question:**

1. Using Eq (4.6), show that Eq (4.8) is a solution of Eq (4.7).

2. Express \( E^{(0)} \) of Eq (4.7) by \( E_{1s} \) of Eq (4.6). How do you explain this in terms of the assumed relation between the two electrons?

3. Let us define \( E_H = -\hbar c R_H = -13.60 \text{ eV} \), the 1s electronic energy of hydrogen atom \((Z = 1)\). Express \( E_{1s} \) by \( E_H \) and \( Z \).

Now, the basic idea of the 1st-order perturbation theory is to employ this approximate (0th order) wave function to evaluate the total energy

\[
E \simeq \langle \psi^{(0)} | H | \psi^{(0)} \rangle = \langle \psi^{(0)} | (H_0 + H') | \psi^{(0)} \rangle = E^{(0)} + \langle \psi^{(0)} | H' | \psi^{(0)} \rangle
\]

By using the 1s wave function for the H-like atoms,

\[
\chi_{1s}(r) = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-Zr/a_0}
\]

in which \( a_0 \) is the Bohr radius, we can explicitly write the second term as

\[
E^{(1)} = \langle \psi^{(0)} | H' | \psi^{(0)} \rangle = \frac{1}{\pi^2} \left( \frac{Z}{a_0} \right)^6 \int \int \frac{e^2}{r_1 r_2} e^{-2Z(r_1+r_2)/a_0} dr_1 dr_2
\]

\*\*We are neglecting here the spin of the electrons, or implicitly assuming that the two electrons have different (anti-parallel) spins.

\*\*\*The superscript (0) means that \( \psi^{(0)} \) and \( E^{(0)} \) correspond to the non-interacting Hamiltonian \( H_0 \).

\*\*In this lecture course, it is sufficient to consider that the Dirac’s bra-ket is a notational simplification of the integral over the space coordinates, i.e.,

\[
\langle \Psi | \hat{A} | \Phi \rangle = \int \Psi^* \hat{A} \Phi \, dx
\]
The calculation is rather elaborate though well-defined; \(\dagger\dagger\) the result is

\[ E^{(1)} = -\frac{5}{4} Z E_H. \]  

(4.12)

Therefore,

\[ E \simeq E^{(0)} + E^{(1)} = (2Z^2 - \frac{5}{4} Z) E_H = \frac{11}{2} E_H = -74.80 eV \]  

(4.13)

In the last two, we have put \(Z = 2\) for helium.

### 4.3 Variational method

The other representative approximation method, the variational method, is rather different from the perturbation method. Let us see how it works on the same problem of the electronic energy of helium atom.

Considering that the (Aufbau) form of Eq (4.8)

\[ \psi^{(0)}(r_1, r_2) = \chi_{1s}(r_1)\chi_{1s}(r_2) = \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-Z(r_1+r_2)/a_0} \]  

(4.14)

would be a good starting point, we assume an analogous form for the trial function

\[ \phi_\alpha(r_1, r_2) = \frac{1}{\pi} \left( \frac{\alpha}{a_0} \right)^3 e^{-\alpha(r_1+r_2)/a_0} \]  

(4.15)

in which the nuclear charge \(Z\) has been replaced by a variable parameter \(\alpha\). We then seek for the best value of \(\alpha\). This \(\alpha\) can be considered as the effective nuclear charge which takes account of the shielding effect by the other electron(s) of the bare nuclear charge \(Z\).

**Question:** What was the fundamental assumption to derive Eq (4.8) in the previous subsection? (This way of describing the many-electron wave functions by a product of one-electron orbitals is called “independent particle approximation”.)

The trial wave function \(\phi_\alpha\) attempts to take account of the electron-electron interaction in the form of the shielded effective nuclear charge. This shielding effect will result in the optimal \(\alpha\) somehow smaller than \(Z\). As seen in Eq (4.10) with \(Z\) replaced by \(\alpha\), the smaller nuclear charge \(\alpha\) means that the electron orbital is expanded in space. This expansion can be regarded as a consequence of the electron-electron repulsion effect.

\(\dagger\dagger\) See, Atkins & Friedman, Sec 7.8; Pauling & Wilson, Sec 23b and Appendix V.
The problem is now to find the optimal value of the parameter $\alpha$. The **variational theorem** states that the exact ground state energy is always lower than the energy from the approximate trial wave function. This means that the best approximation should be obtained by **minimizing**

$$E(\alpha) = \langle \phi_\alpha | H | \phi_\alpha \rangle$$

as a function of the parameter $\alpha$. The calculation of this integral is very similar to that of Eq (4.11). The result is 

$$E(\alpha) = (-2\alpha^2 + 4Z\alpha - \frac{5}{4}\alpha)E_H$$

This simple quadratic function of $\alpha$ has a single minimum (note that $E_H < 0$) which determines the variationally best $\alpha$.

**Question**: Find the minimum of $E(\alpha)$. Is the value of $\alpha$ at the minimum larger or smaller than $Z$? How do you interpret it?

<table>
<thead>
<tr>
<th></th>
<th>1st-order Perturbation</th>
<th>Variation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (eV)</td>
<td>-74.80</td>
<td>-77.45</td>
<td>-78.98</td>
</tr>
<tr>
<td>IP (eV)</td>
<td>20.40</td>
<td>23.05</td>
<td>24.58</td>
</tr>
</tbody>
</table>

**4.4 Summary: Perturbation Theory (time-independent)**

In this section, we only summarize without the derivation the general results of the time-independent perturbation theory. The derivation is via a straightforward (though slightly tedious) algebra as described in the textbooks.

Assume: the solutions $\psi_n^{(0)}$ and $E_n^{(0)}$ for the reference Hamiltonian $H_0$ are known:

$$H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad (n = 0, 1, 2, \cdots)$$

Then, a small perturbation energy $V$ is added to $H_0$: $H = H_0 + V$. (In other words, we divide the full Hamiltonian $H$ into the known part $H_0$ and the rest $V$.) Now we want the (approximate) solution of

$$H\psi_n = E_n\psi_n \quad (n = 0, 1, 2, \cdots)$$

\[\text{††} \text{Confirm that this reduces to Eq (4.12) when } \alpha = Z.\]

\[\text{*See, Atkins & Friedman, Sec 6.2-6.5; Pauling & Wilson, Sec 23, 25.}\]
based on the knowledge of the solutions of Eq (4.18) for $H_0$. The perturbation theory answers to this as

$$E_n = E_n^{(0)} + \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle + \sum_{k \neq n} \frac{\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle^2}{E_n^{(0)} - E_k^{(0)}} + \cdots$$  \hspace{1cm} (4.20)

$$\psi_n = \psi_n^{(0)} + \sum_{k \neq n} \frac{\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \psi_k^{(0)} + \cdots$$  \hspace{1cm} (4.21)

These formulas indicate that the change of the wave function from the reference $\psi_n^{(0)}$ due to the perturbation $V$ is described by the mixing of the other functions $\psi_k^{0}$. The mixing coefficient is proportional to the integral of the perturbation energy $V$ sandwiched by these functions, $\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle$. This integral represents the coupling strength between these reference states, and is called the ‘transition matrix element’. It is also seen in Eq (4.21) that the mixing is proportional to $(E_n^{(0)} - E_k^{(0)})^{-1}$, which means that two states mix better when their energies are closer.

The corrected energy Eq (4.20) has somehow an analogous form: the transition matrix elements in the numerator (note however that they are the absolute squares) and the energy difference in the denominator. These terms are the second-order perturbation corrections which was not considered in the helium example in the previous section. The application of the second-order perturbation theory to the polarizability of molecules is discussed in Sec 7.

**Note:** The theory breaks down when there exist energy degeneracies, i.e., when a pair or pairs of the reference states has the same energy, $E_n^{(0)} = E_k^{(0)}$. This is easily seen in the formulas containing the energy differences in the denominator. The degenerate cases should be treated in a different way, which will be out of the scope of this lecture course. †

### 4.5 Summary: Variational Theorem

In this section, we summarize the variational theorem together with a short proof. The theorem itself is very simple and easy to appreciate or memorize. The proof is also fairly compact, although it requires the knowledge and understanding of the concept of completeness and orthonormality of the eigenfunctions of Hermite operators that include Hamiltonians. However, this lecture course does not require complete understanding of these mathematical jargons and the proof of the theorem, because

---

†See, Atkins & Friedman, Sec 6.8; Pauling & Wilson, Sec 24.
they are not essential for the rest of the materials where the major aims are to see how the method can be applied to chemical problems. More thorough description of the theorem with applications can be found in the textbooks.

Suppose we are to evaluate the ground state energy $E_0$ of a Hamiltonian $H$. From some physical intuitions or model considerations, we set up a trial wave function $\phi$ which contains some variable parameters. The variational theorem guarantees that the energy expectation value from any trial wave functions will never be lower than the exact energy $E_0$

$$E_0 \leq \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}, \quad \phi = \text{trial function} \tag{4.22}$$

(Note the existence of the denominator in the right hand side.\(^\S\)) Therefore, the best approximation is obtained by minimizing the right hand side within the parameter space of the trial function.

**Proof:** Suppose that the exact solutions are $\psi_n$ and $E_n$:

$$H \psi_n = E_n \psi_n \quad (n = 0, 1, 2, \cdots) \tag{4.23}$$

Of course, we don’t know what they are (otherwise we don’t need to attempt the approximate calculations at all!). However, we know that the exact wave functions constitute a complete orthonormal set, which means that we can describe any functions (in the same coordinate space under consideration) in terms of a linear combination of this set $\{\psi_n\}$. We can thus express our trial wave function as

$$\phi = \sum_{n=0}^{\infty} c_n \psi_n \tag{4.24}$$

\(^\dagger\) See, Atkins & Friedman, Sec 6.9; Pauling & Wilson, Sec 26.

\(^\S\) We did not include the denominator $\langle \phi | \phi \rangle$ previously in Eq (4.16). This was because the functional form of Eq (4.15) automatically guarantees that the wave function is normalized, i.e., $\langle \phi_n | \phi_n \rangle = 1$, for any value of the parameter $\alpha$. However, this is not always the case for general trial functions. For example, the LCAO wave functions (to be treated in the next section) are not normalized as they are, so long as we treat the coefficients as free parameters. We therefore need the denominator in Eq (4.22) in order to normalize the expectation value of the Hamiltonian $H$. 

21
Then, the expectation value of $H$ over $\phi$ and the exact energy $E_0$ are compared as
\[
\langle \phi | H | \phi \rangle - E_0 \langle \phi | \phi \rangle = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} c_n^* c_m \langle \psi_n | H - E_0 | \psi_m \rangle = \sum_{n} \sum_{m} c_n^* c_m (E_n - E_0) \delta_{nm} = \sum_{n} |c_n|^2 (E_n - E_0) \geq 0 \quad (\Leftarrow \text{because } E_0 \text{ is the lowest of } E_n)
\]

And because $\langle \phi | \phi \rangle = \int |\phi|^2 dx \geq 0$, we find that Eq (4.22) is true.

**Note:** $\delta_{nm} = 1$ when $n = m$, and otherwise 0. (This is called the Kronecker’s delta)

$\{\psi_n\}$ is an orthonormal set $\iff \langle \psi_n | \psi_m \rangle = \delta_{nm}$

## 5 LCAO-MO Method

### 5.1 Diatomic molecule

One of the major advantages of the variational method is its versatility. We can employ any form of the trial function so long as it is physically sensible. The quality of the approximation solely depends on the choice of the trial function.

The most straightforward and general form of the trial function would be a linear combination of some appropriate set of basis functions $\{f_i\}$

\[
\phi(x) = \sum_i c_i f_i(x) \quad (5.1)
\]

The coefficients $c_i$ are then taken to be the variational parameters. The central application of this idea in chemistry is the LCAO-MO method, molecular orbitals (MOs) formed by a linear combination of atomic orbitals (AOs).

Let us consider, for example, a diatomic molecule A-B. We also assume, for simplicity, that the atoms A and B each contribute one electron in AOs $\chi_A$ and $\chi_B$ to form a covalent bond A-B. The molecular orbital in the LCAO-MO method is then described as

\[
\phi = c_A \chi_A + c_B \chi_B \quad (5.2)
\]
We further assume that $c_A$ and $c_B$ are real numbers, and $\chi_A$ and $\chi_B$ are normalized, i.e., $\langle \chi_A | \chi_A \rangle = \langle \chi_B | \chi_B \rangle = 1$. At this stage they are not necessarily orthogonal to each other, namely, the overlap integral may be finite, $S_{AB} = \langle \chi_A | \chi_B \rangle \neq 0$. The expectation values of the Hamiltonian $H$ over the AOs, e.g., $H_{AA} = \langle \chi_A | H | \chi_A \rangle$, represent the atomic energies. These may be computed numerically as in Eq (4.11), or be estimated from spectroscopic experiments, or may be simply taken as empirical parameters (as in the Hückel theory). The integral of $H$ sandwiched by the different AOs, $H_{AB} = \langle \chi_A | H | \chi_B \rangle$, is called the “transfer energy” or “resonance energy” that describes the electron delocalization effect over the two AOs.

Now we express the expectation value of the Hamiltonian over the MO $\phi$ in terms of the AO integrals $H_{AA}, H_{BB}$ and $H_{AB}$:

$$\langle \phi | H | \phi \rangle = c_A^2 H_{AA} + c_A c_B (H_{AB} + H_{BA}) + c_B^2 H_{BB} \quad (5.3)$$

Similarly, the self-overlap integral is expressed as

$$\langle \phi | \phi \rangle = c_A^2 + c_A c_B (S_{AB} + S_{BA}) + c_B^2 \quad (5.4)$$

Our task is to find the best MO coefficients $c_A$ and $c_B$ from the variational principle. To this end, we consider the variation of the energy expectation value $E$

$$E = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \quad (5.5)$$

as a function of these parameters $c_A$ and $c_B$. Remember that the denominator $\langle \phi | \phi \rangle$ is needed because $\phi$ is not necessarily normalized to unity as it contains the unknown parameters $c_A$ and $c_B$. (See the footnote in Sec 4.5.)

According to the variational method, we search the optimal values of $c_A$ and $c_B$ that minimize $E$. The necessary conditions are $\partial E / \partial c_A = \partial E / \partial c_B = 0$. Although it is possible to differentiate Eq (5.6) directly, it would be rather easier to first rearrange it as

$$\text{Eq (5.6)} \Rightarrow E \langle \phi | \phi \rangle - \langle \phi | H | \phi \rangle = 0 \quad (5.6)$$

Then, by differentiating with respect to $c_A$,

$$\frac{\partial E}{\partial c_A} \langle \phi | \phi \rangle + E \frac{\partial}{\partial c_A} \langle \phi | \phi \rangle - \frac{\partial}{\partial c_A} \langle \phi | H | \phi \rangle = 0 \quad (5.7)$$

Using Eqs (5.3) and (5.4),

$$\frac{\partial E}{\partial c_A} \langle \phi | \phi \rangle + E (2c_A + 2c_B S_{AB}) - (2c_A H_{AA} + 2c_B H_{AB}) = 0 \quad (5.8)$$
Applying the stationary condition $\partial E/\partial c_A = 0$ and rearranging the terms,

$$(H_{AA} - E)c_A + (H_{AB} - ES_{AB})c_B = 0$$  (5.9)

Similarly, from $\partial E/\partial c_B = 0$,

$$(H_{BA} - ES_{BA})c_A + (H_{BB} - E)c_B = 0$$  (5.10)

Combining these two into a matrix form,

$$\begin{bmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - E \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$  (5.11)

This may be written in an abstract and general form,

$$(H - ES) c = 0$$  (5.12)

Now, in order to have non-zero solutions $c \neq 0$, it is necessary that the determinant of the matrix $H - ES$ vanishes.

$$|H - ES| = 0$$  (5.13)

(Otherwise the inverse matrix $(H - ES)^{-1}$ exists, which is then multiplied to Eq (5.12) from the left to give $c = (H - ES)^{-1} 0 = 0$.) Eq (5.13) gives the condition to determine the MO energy $E$ and is called the Secular Equation. After determining the value(s) of $E$, we put it back into the matrix equation (5.11), from which the coefficients $c_A$ and $c_B$ can be determined.

If we employ from the beginning a set of orthonormal AOs, i.e., $\langle \chi_A | \chi_B \rangle = 0$ for $A \neq B$, then the overlap matrix is the unit matrix, $S = I$ and the matrix equation (5.12) is simplified as

$$(H - EI) c = 0 \Rightarrow Hc = Ec$$  (5.14)

Namely, the problem reduces to the matrix eigenvalue problem. The matrix eigenvalue equation can be solved by the matrix-diagonalisation procedure which is nowadays very straightforward on computers.

More precisely, what we can determine is only the ratio $c_A : c_B$ because the two lines of Eq (5.11) becomes equivalent to each other such that we essentially have only one equation for $c_A$ and $c_B$. Indeed, this is exactly what the secular equation (5.13) imposes to the matrix equation. Namely, the consequence of the secular equation is to collapse the two lines from Eq (5.11) in the $c_A$-$c_B$ coordinate plane. After determining the ratio $c_A : c_B$, the normalization condition $\langle \phi | \phi \rangle = 1$ specifies the numbers for $c_A$ and $c_B$. See Eq (5.4).
5.2 Generalization

In the previous section, we started with a simple $2 \times 2$ problem, i.e., the LCAO-MO formed by two AOs. Obviously, as suggested by the general matrix formula (5.12), the discussion can be straightforwardly generalized to arbitrary number ($N$) of the basis (AO) functions:

$$\phi = \sum_{i=1}^{N} c_i \chi_i$$  \hspace{1cm} (5.15)

Moreover, as would be easily inferred, this procedure is not bound to the LCAO-MO problem. General problems, in which the trial wave function may be modelled by a linear combination of a (sensible) set of basis functions, can be handled analogously in terms of the secular equation.

5.3 Hückel MO theory

One of the simplest treatment of the $\pi$ MOs of conjugate planer hydrocarbons is the Hückel MO method, in which we only consider one $\pi$ electron per carbon atom and describe the $\pi$ MOs as a linear combination of these $2p\pi$ AOs. We further introduce the following simplifying assumptions:

- The $2p\pi$ AOs are orthogonal to each other and normalized (i.e., orthonormal basis functions that give $S = I$).

- All the diagonal elements of the Hamiltonian matrix are represented by a single parameter $\alpha$, i.e., $H_{11} = H_{22} = \cdots = \alpha$. This is the energy of the carbon $2p\pi$ AO.

- The off-diagonal matrix elements are set to be another common parameter $H_{ij} = \beta$ only when the carbon atoms $i$ and $j$ are connected; otherwise $H_{ij} = 0$.

The first assumption is valid only approximately: Obviously, neighbouring carbon $2p\pi$ AOs have a finite overlap, though much smaller than the overlap between the $2p\sigma$ AOs. The second assumption implies that the diagonal energy is an intrinsic atomic quantity, and that its dependence on the chemical environment may be neglected. Because of this and the third assumption, the Hückel method does not distinguish between any conformational isomers, e.g., cis- and trans- forms of linear polyenes.
For example, the Hückel Hamiltonian matrix for butadiene is given by

\[
H = \begin{bmatrix}
\alpha & \beta & 0 & 0 \\
\beta & \alpha & \beta & 0 \\
0 & \beta & \alpha & \beta \\
0 & 0 & \beta & \alpha
\end{bmatrix}
\] (5.16)

Obviously, this does not distinguish cis- and trans-butadienes. The secular equation is

\[
\det \begin{bmatrix}
\alpha - \epsilon & \beta & 0 & 0 \\
\beta & \alpha - \epsilon & \beta & 0 \\
0 & \beta & \alpha - \epsilon & \beta \\
0 & 0 & \beta & \alpha - \epsilon
\end{bmatrix} = 0
\] (5.17)

It is not too difficult to solve this equation by hand if you know, for example, the method of Laplace expansion by cofactors. However, because this procedure is well-defined, it is very straightforwardly handled by computers these days.

**Question:**

1. Calculate the Hückel MO energies and coefficients for ethylene (C\textsubscript{2}H\textsubscript{4}) and allyl cation (C\textsubscript{3}H\textsubscript{5}\textsuperscript{+}).

2. Write down the Hückel Hamiltonian of benzene (C\textsubscript{6}H\textsubscript{6}) and hexatriene (C\textsubscript{6}H\textsubscript{12}). How do they differ?

**Note:** We can generalize the method to include the hetero-atoms (e.g., N, O) by introducing different parameters (e.g., \(\alpha_N, \beta_{CN}\) etc.). It is also possible to take account of the \(\sigma\) bonds. The generalized theory is called the ‘extended Hückel’ method, which played an important role for the discovery of the Woodward-Hoffman rule and the Frontier MO theory.

### 6 Variation-perturbation method

Let us come back to Eq (5.14) in the orthogonal basis \((S = I)\)

\[
Hc = Ec
\] (6.1)

or equivalently, the secular equation

\[
|H - EI| = 0
\] (6.2)
As we have seen in the examples of the Hückel theory, this is in general an $N$-th order polynomial equation for the unknown $E$, where $N$ is the number of the AO basis functions, and therefore not very easy to solve analytically. However, there is a technique to obtain approximate solutions. The approximation is valid when the off-diagonal matrix elements $H_{ij}$ are small compared to the diagonals $H_{ii}$. Small off-diagonal $H_{ij}$ means that the interaction, or the mixing, between the $i$th and $j$th basis functions is small. For example, in LCAO-MO method, small $H_{ij}$ means that the interaction between the electrons in the AOs $\chi_i$ and $\chi_j$ is small, and therefore, the modification of the energy due to the interaction is small. In this case, the electronic energy levels are not much different from the original AO energies $H_{ii}$ and $H_{jj}$. The energy levels with these small corrections are then given by

$$E_n \simeq H_{nn} + \sum_{k \neq n} \frac{H_{nk} H_{kn}}{H_{nn} - H_{kk}} + \cdots$$

(6.3)

The derivation is related to the concept of ‘effective Hamiltonian’, which is outlined in Appendix B.** However, instead of diving into the mathematical details, let us note here that this formula is reminiscent of the ordinary perturbation theory in Sec 4.4

$$E_n = E_n^{(0)} + \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle + \sum_{k \neq n} \frac{|\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}} + \cdots$$

(6.4)

Indeed, the integral $\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle$ is called the matrix element of $V$ in the basis set $\{\psi_i^{(0)}\}$, and is often written as $V_{nk}$. Its complex conjugate is given by exchanging $n$ and $k$ such that $\langle \psi_n^{(0)} | V | \psi_k^{(0)} \rangle^* = \langle \psi_k^{(0)} | V | \psi_n^{(0)} \rangle$, that is, $V_{nk}^* = V_{kn}$. Therefore, $|V_{nk}|^2 = V_{nk} V_{kn}$ which makes clearer the correspondence between Eqs (6.3) and (6.4).

**Non-orthogonal case:** When the basis functions are non-orthogonal, $S \neq I$, the secular equation is written as

$$Hc = ESc \quad \Rightarrow \quad |H - ES| = 0$$

(6.5)

The variational perturbation formula is slightly modified accordingly (see Appendix B)

$$E_n \simeq H_{nn} + \sum_{k \neq n} \frac{|H_{nk} - S_{nk} H_{nn}|^2}{H_{nn} - H_{kk}} + \cdots$$

(6.6)

When there are degenerate diagonal elements, $H_{nn} = H_{kk}$, Eq (6.3) cannot be used because the denominator diverges. This means that the method cannot be used for the ordinary Hückel Hamiltonian where $H_{ii} = \alpha$ for all the diagonal elements. Typical applications of the method are discussed in the next section.

**See also, Pauling & Wilson, Sec 27a.
6.1 Application: Charge-transfer complex

6.1.1 Intermolecular CT spectra

Example 1: I$_2$ in benzene $\Rightarrow$ new absorption ($\sim$300nm) absent in benzene or I$_2$ alone.
Example 2: mixture of colorless organic liquids $\Rightarrow$ colors

<table>
<thead>
<tr>
<th>picric acid</th>
<th>+ benzene</th>
<th>$\Rightarrow$ yellow</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ naphtalene</td>
<td>$\Rightarrow$ dark yellow</td>
<td></td>
</tr>
<tr>
<td>+ anthracene</td>
<td>$\Rightarrow$ red</td>
<td></td>
</tr>
<tr>
<td>+ naphtacene</td>
<td>$\Rightarrow$ red</td>
<td></td>
</tr>
</tbody>
</table>

Mulliken’s CT complex: “Resonance” $A \cdot D \leftrightarrow A^- \cdot D^+$

$$\Psi \simeq c_1 \psi_1 (A \cdot D) + c_2 \psi_2 (A^- \cdot D^+)$$

Non-orthogonal variational perturbation theory

$$E \simeq H_{11} + \frac{|H_{12} - S_{12}H_{11}|^2}{H_{11} - H_{22}}$$

(6.8)

Namely, the energy of $\psi_1 (A \cdot D)$ is stabilized by

$$\Delta E(\text{CT}) \equiv E - H_{11} \simeq \frac{|H_{12} - S_{12}H_{11}|^2}{H_{11} - H_{22}}$$

due to the mixing of the CT state $\psi_2 (A^- \cdot D^+)$. Note that $\Delta E(\text{CT}) < 0$ because $H_{11} - H_{22} < 0$.

Correlation to the Ionization Potential and Electron Affinity:

$$H_{22} - H_{11} \simeq \text{IP}(D) - \text{EA}(A)$$

Usually, IP > EA for neutral molecules; for example, IP of organic molecules are typically around several eV, while the EA is less than 1 eV. Therefore, CT interaction is large when the IP of the electron donor is small and the EA of the acceptor is large; this simply means that the charge transfer is energetically favorable.
Correlation with the Orbital Overlap: \( H_{12} \propto S_{12} \) (approximately)

\[
\Delta E(\text{CT}) \propto |S_{12}|^2 = |\langle \psi_1(A \cdot D)|\psi_2(A^- \cdot D^+) \rangle|^2 \\
\simeq |\langle \varphi_D(\text{HOMO})|\varphi_A(\text{LUMO}) \rangle|^2
\]

Example: Structure of ion-molecule complex

\[
\begin{array}{c}
\text{Ag} \cdots \text{benzene complex} \\
\text{LUMO} = 5s \\
\text{(spherical)} \\
\text{HOMO} = \square
\end{array}
\Rightarrow \begin{array}{c}
\text{Ag} \\
\text{Ag}
\end{array}
\]

6.2 Application: Frontier MO theory

Molecule A:

- MO \( \phi_i = \sum_r c_{ir} \chi_r \) (MO index \( i \), AO index \( r \))
- MO energies \( E_i \) (ie, \( \langle \phi_i|h_A|\phi_i' \rangle = E_i \delta_{ii'} \) )

Molecule B:

- MO \( \phi_k = \sum_s c_{ks} \chi_s \) (MO index \( k \), AO index \( s \) )
- MO energies \( E_k \) (ie, \( \langle \phi_k|h_B|\phi_k' \rangle = E_k \delta_{kk'} \) )

Interaction energy:

According to the variational perturbation theory, the energy change of the \( i \)th MO energy of molecule A due to interaction with B is given by

\[
\delta E_i = \sum_{k \in B} \frac{|h'_{ik}|^2}{E_i - E_k}
\] (6.9)

in which the summation is over all the MOs (occupied and unoccupied) of molecule B. \( h'_{ik} \equiv \langle \phi_i|h'|\phi_k \rangle \) represents the interaction energy between the MOs \( \phi_i \) in molecule A and \( \phi_k \) in molecule B. Similarly, the energy change of the \( k \)th MO energy of molecule B due to interaction with A is

\[
\delta E_k = \sum_{i \in A} \frac{|h'_{ik}|^2}{E_k - E_i}
\] (6.10)
The total energy change is

$$\Delta E = 2 \sum_{i}^{\text{occ}} \delta E_i + 2 \sum_{k}^{\text{occ}} \delta E_k = 2 \left( \sum_{i}^{\text{occ}} \sum_{k}^{\text{all}} - \sum_{i}^{\text{occ}} \sum_{k}^{\text{occ}} \right) \frac{|h'_{ik}|^2}{E_i - E_k}$$

(6.11)

in which the factor 2 takes account of the occupation of up and down spins. As derived in Appendix C, this is converted to a form that represent interaction between occupied and unoccupied MOs. That is, the molecular interaction is described in terms of the electron delocalization from the occupied MOs of one molecule to the unoccupied MOs of the other.

Moreover, assuming that the terms with small denominator are dominant, $\Delta E$ is approximated by the HOMO-LUMO interaction

$$\Delta E \approx 2 \frac{|h'_{\text{HO(A),LU(B)}}|^2}{E_{\text{HO(A)}} - E_{\text{LU(B)}}} - 2 \frac{|h'_{\text{LU(A),HO(B)}}|^2}{E_{\text{LU(A)}} - E_{\text{HO(B)}}}$$

(6.12)

This is the basis of the Frontier MO (FMO) theory. Remember that the matrix element $h'_{ik}$ is based on the MOs rather than AOs. By using the LCAO-MO expansions $\phi_i = \sum_r c_{ir} \chi_r$ and $\phi_k = \sum_s c_{ks} \chi_s$, and the defining the interaction energy in terms of the AOs, $\beta_{rs} \equiv \langle \chi_r | h' | \chi_s \rangle$, we get

$$h'_{ik} = \sum_r \sum_s c_{ir} c_{ks} \beta_{rs}$$

(6.13)

In Eq (6.12), the MO pair $(i, k)$ is represented by the HOMO and LUMO of molecules A and B, such that the coefficients $c_{ir}$ and $c_{ks}$ for the HOMO and LUMO, i.e., $(i, k) = (\text{HO(A)}, \text{LU(B)})$ and $(\text{LU(A)}, \text{HO(B)})$, determine the molecular interaction. In this way, we particularly look at the HOMO-LUMO coefficients in the FMO theory.
7 Electronic polarizability

7.1 Quantum mechanical expression

We come back to the perturbation theory summarized in Sec 4.4. In the treatment of helium atom in Sec 4.1, we only considered the 1st-order perturbation just to illustrate the basic idea. The 2nd-order perturbation theory would be, on the other hand, best illustrated in chemistry by the application to electronic polarizability of molecules.

For simplicity, we first consider a diatomic molecule A-B which has a permanent dipole \( \mu \). We then place this diatomic in a uniform electric field of strength \( \epsilon \) directed parallel to the bond axis. The field will induce rearrangement of the charge distribution and alter the molecule’s dipole moment \( \mu \) such as

\[
\mu \rightarrow \mu + \alpha \epsilon + \frac{1}{2} \beta \epsilon^2 + \cdots \tag{7.1}
\]

in which the coefficients \( \alpha \) and \( \beta \) are called polarizability and hyperpolarizability. The energy of the molecule also changes as (see Appendix D)

\[
E \rightarrow E - \mu \epsilon - \frac{1}{2} \alpha \epsilon^2 - \frac{1}{3!} \beta \epsilon^3 + \cdots \tag{7.2}
\]

Comparing this with the Taylor expansion of the energy \( E \) as a function of the field strength \( \epsilon \)

\[
E(\epsilon) = E(0) + \left( \frac{dE}{d\epsilon} \right)_0 \epsilon + \frac{1}{2} \left( \frac{d^2E}{d\epsilon^2} \right)_0 \epsilon^2 + \frac{1}{3!} \left( \frac{d^3E}{d\epsilon^3} \right)_0 \epsilon^3 + \cdots \tag{7.3}
\]

we find

\[
\mu = -\left( \frac{dE}{d\epsilon} \right)_0, \quad \alpha = -\left( \frac{d^2E}{d\epsilon^2} \right)_0, \quad \beta = -\left( \frac{d^3E}{d\epsilon^3} \right)_0 \tag{7.4}
\]

The subscript 0 means the derivatives at \( \epsilon = 0 \).
Now let us consider this problem in quantum mechanics. To compare with the above formula, we consider the energy change of the molecule under the electric field. We start by assuming that we already know the solution of the Schrödinger equation without the field

\[ H_0 \phi_n = E^{(0)}_n \phi_n \quad (n = 0, 1, 2, \cdots) \tag{7.5} \]

(Note the different notation from Sec 4.4. Here we use \( \phi_n \) rather than \( \psi^{(0)}_n \) for notational simplicity.) Now, by applying the electric field, the Hamiltonian changes

\[ H_0 \rightarrow H_0 + V \tag{7.6} \]

We will specify later how this interaction \( V \) is described in terms of the molecular properties and the field strength \( \epsilon \). But before doing it, let us write down the perturbation theoretical expression of the energy change due to this additional interaction \( V \) (see Eq (4.20))

\[ E_n = E^{(0)}_n + \langle \phi_n | V | \phi_n \rangle + \sum_{k \neq n} \frac{|\langle \phi_n | V | \phi_k \rangle|^2}{E^{(0)}_n - E^{(0)}_k} + \cdots \tag{7.7} \]

The remaining task is to express the interaction \( V \) in terms of \( \epsilon \) and then compare with Eq (7.4) to find the quantum mechanical expression for the polarizability.

The interaction of the molecule with the electric field is given by

\[ V = -\mu \epsilon \tag{7.8} \]

By putting this into Eq (7.7), we get

\[ E_n = E^{(0)}_n - \langle \phi_n | \mu | \phi_n \rangle \epsilon + \sum_{k \neq n} \frac{|\langle \phi_n | \mu | \phi_k \rangle|^2}{E^{(0)}_n - E^{(0)}_k} \epsilon^2 + \cdots \tag{7.9} \]

Comparing this with Eq (7.4) we find

\[ \alpha = -2 \sum_{k \neq n} \frac{|\langle \phi_n | \mu | \phi_k \rangle|^2}{E^{(0)}_n - E^{(0)}_k} \tag{7.10} \]

The quantity \( \langle \phi_n | \mu | \phi_k \rangle \) is called **transition dipole moment**, which also plays a key role in molecular spectroscopy.

**Notes:**
1. The molecular dipole moment is a vector given by a sum of the position vectors multiplied by the charges of all the particles (electrons and nuclei)

\[ \mu = e \sum_l Z_l \mathbf{R}_l - e \sum_i \mathbf{r}_i \quad (7.11) \]

2. † To simplify the argument, we have neglected the relative directions of the dipole moment and the applied field. In general, the induced dipole is not necessarily parallel to the field, so that the polarizability is a $3 \times 3$ matrix (or tensor)

induced dipole: \( \mu' = \alpha \cdot \mathbf{E} \) or

\[
\begin{pmatrix}
\mu'_x \\
\mu'_y \\
\mu'_z
\end{pmatrix} =
\begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix} \quad (7.12)
\]

7.2 Closure approximation

7.2.1 Preparation

The integral \( \langle \phi_i | A | \phi_j \rangle \) is often called the matrix element \( A_{ij} \) of operator \( A \) in the basis \( \{ \phi_i \} \). Although the dimension of this ‘matrix’ may be infinite, since there can be infinite number of energy levels and thus wave functions \( \{ \phi_i \} \), we consider (or define) their algebra analogously to the ordinary matrix algebra. So, analogously to the ordinary matrix multiplication

\[ (AB)_{ij} = \sum_k A_{ik} B_{kj} \quad (7.13) \]

applies the following algebra for the integrals

\[ \langle \phi_i | AB | \phi_j \rangle = \sum_k \langle \phi_i | A | \phi_k \rangle \langle \phi_k | B | \phi_j \rangle \quad (7.14) \]

**Note**: This also suggests a symbolic relation

\[ \sum_k | \phi_k \rangle \langle \phi_k | = 1 \quad (7.15) \]

which is called “completeness relation”.

33
7.2.2 Hermite operator

One more preparation for the main topic of this subsection. By construction, the wave functions are generally complex functions, i.e., have real and imaginary parts. Quantum mechanics also postulates that all the observable physical quantities are represented by Hermite operators which satisfy for any wave functions Ψ and Φ

\[ \langle \Psi | \hat{\Omega} | \Phi \rangle = \langle \Phi | \hat{\Omega} | \Psi \rangle^* \quad \text{(or } = \langle \hat{\Omega} \Psi | \Phi \rangle \text{)} \quad (7.16) \]

We can show that the eigenvalues of Hermite operators are always real. (In other words, we postulate that physical observables are associated with Hermite operators because they give real eigenvalues.) More details are given in textbooks, but in fact all we need here is just

\[ |\langle \phi_n | V | \phi_k \rangle|^2 = \langle \phi_n | V | \phi_k \rangle \langle \phi_n | V | \phi_k \rangle^* = \langle \phi_n | V | \phi_k \rangle \langle \phi_k | V | \phi_n \rangle \quad (7.17) \]

7.2.3 Closure approximation

Now, let us look at the 2nd-order term in Eq (7.7). It contains Eq (7.17) in the numerator, so at first sight we might think of using Eq (7.14). However, we can’t because the denominator also depends on the summation index \( k \).

For the reason to be explained shortly, let us consider the ground state energy with \( n = 0 \):

\[ E_0 = E_0^{(0)} + \langle \phi_0 | V | \phi_0 \rangle + \sum_{k \neq 0} \frac{|\langle \phi_0 | V | \phi_k \rangle|^2}{E_0^{(0)} - E_k^{(0)}} + \cdots \quad (7.18) \]

As is often observed, the electronic ground state energy \( E_0^{(0)} \) is usually well separated from the excited state energies. Then, the denominator \( E_0^{(0)} - E_k^{(0)} \) may be represented by a constant \( \Delta E \) and approximately factored out

\[ E_0 \simeq E_0^{(0)} + \langle \phi_0 | V | \phi_0 \rangle - \frac{1}{\Delta E} \sum_{k \neq 0} |\langle \phi_k | V | \phi_0 \rangle|^2 \quad (7.19) \]

so we can make use of Eqs (7.17) and (7.14)

\[ \sum_{k \neq 0} |\langle \phi_k | V | \phi_0 \rangle|^2 = \sum_{k \neq 0} \langle \phi_0 | V | \phi_k \rangle \langle \phi_k | V | \phi_0 \rangle = \sum_k \langle \phi_0 | V | \phi_k \rangle \langle \phi_k | V | \phi_0 \rangle - \langle \phi_0 | V | \phi_0 \rangle \langle \phi_0 | V | \phi_0 \rangle \quad (7.20) \]

\[ = \langle \phi_0 | V^2 | \phi_0 \rangle - \langle \phi_0 | V | \phi_0 \rangle^2 \]

34
Introducing notations such as $\langle \phi_0 | V | \phi_0 \rangle = \langle V \rangle_0$ etc. we finally get

$$E_0 \simeq E_0^{(0)} + \langle V \rangle_0 + \frac{1}{\Delta E} \langle \delta V^2 \rangle_0$$  \hspace{1cm} (7.21)

where $\delta V \equiv V - \langle V \rangle_0$ is the deviation of $V$ from its average $\langle V \rangle_0$, and $\langle \delta V^2 \rangle_0 = \langle V^2 \rangle_0 - \langle V \rangle_0^2$ is the mean-squares fluctuation of $V$.

**Question:** Confirm the derivation through Eqs (7.20)-(7.21).

### 7.2.4 Approximation of polarizability

It is straightforward to apply the closure approximation to the molecular polarizability

$$\alpha \simeq \frac{2}{\Delta E} \langle \delta \mu^2 \rangle_0$$  \hspace{1cm} (7.22)

Therefore, the polarizability is proportional to the mean-squares fluctuation of the dipole moment. It is also seen that the polarizability is large when the electronic excitation energy $\Delta E$ is small. This is in accord with the fact that molecules with $\pi$ electrons generally have high polarizabilities.

Remember that we neglected the anisotropy of the polarizability. What we usually observe is the average of the three directions

$$\bar{\alpha} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$= \frac{2}{3} \frac{\langle \delta \mu^2 \rangle + \mu^2_{y} + \mu^2_{z} \rangle_0}{\Delta E} = \frac{2}{3} \frac{\langle \delta \mu^2 \rangle_0}{\Delta E}$$  \hspace{1cm} (7.23)

We further invoke the following approximations:

1. $\langle \delta \mu^2 \rangle_0 \simeq e^2 \langle \delta r^2 \rangle_0$,
   where $\langle \delta r^2 \rangle_0$ represents the expansion of the electron cloud in the molecule (or simply the size of the molecule)

2. $\Delta E \propto$ the ionization potential (I.P.) of the molecule.

To obtain

$$\bar{\alpha} \propto \frac{e^2 \langle \delta r^2 \rangle_0}{IP}$$  \hspace{1cm} (7.24)

This explains fairly well the qualitative trends in a series of comparable systems.
8 Time-dependent perturbation theory

The previous section have dealt with the interaction of molecules with static electric field. This causes redistribution of the charges in the molecule, as represented by the induced dipole and polarizability. Now, what if the electric field was oscillating in time, such as those in light? In this section we discuss a method to treat this kind of time-dependent interaction, which is closely related to molecular spectroscopies.

8.1 Time-dependent interaction

As in the previous section, we assume that the wave functions are already known for the system without the field, namely, we discuss how the perturbed states can be described in terms of the unperturbed states

\[ H_0 \phi_n = E_n^{(0)} \phi_n \]  

(8.1)

As discussed in Sec 2, these are stationary states that show standing wave oscillation along time

\[ \phi_n e^{-iE_n^{(0)} t/\hbar} \]  

(8.2)

Now we turn on the interaction \( V(t) \), which modifies the Hamiltonian

\[ H = H_0 + V(t) \]  

(8.3)

Because the Hamiltonian now depends on time, we look at the time-dependent Schrödinger equation

\[ i\hbar \frac{\partial}{\partial t} \psi(t) = H \psi(t) \]  

(8.4)

It should be useful to expand this \( \psi(t) \) in terms of the zero-field wave functions Eq (8.2),

\[ \psi(t) = \sum_n c_n(t) \phi_n e^{-iE_n^{(0)} t/\hbar} \]  

(8.5)

From the variation of the coefficient \( c_n(t) \) we can discuss the population change among the states \( \phi_n \) induced by the interaction \( V(t) \). For example, if the system is originally in the ground state \( (n = 0) \), we have \( c_0 = 1 \) and \( c_n = 0 \) for \( n \geq 1 \). We turn on the light whose photon energy matches with the excitation energy to the first excited state \( n = 1 \). As a result, the photon absorption occurs such that \( c_1 \) grows along time while \( c_0 \) decays.
Inserting Eq (8.5) into Eq (8.4), multiplying $\phi_k^*$ from the left and carrying out integration over the particle coordinates with the use of the orthonormality $\langle \phi_k | \phi_n \rangle = \delta_{kn}$ we get
\[
\frac{d}{dt} c_k(t) = -\frac{i}{\hbar} \sum_n V_{kn}(t)e^{i\omega_{kn}t} c_n(t) \quad (8.6)
\]
where $V_{kn}(t) = \int \phi_k(q)^* V(q,t) \phi_n(q) dq = \langle k|V(t)|n \rangle$ and $\omega_{kn} = (E_k^{(0)} - E_n^{(0)})/\hbar$

**Question:** Verify Eq (8.6) for the two-state case where Eq (8.5) consists of two terms $n = 1$ and 2.

**8.2 Two-states resonance**

It would be illustrative to consider a simplest case where the system is described by two basis states, for which Eq (8.6) is
\[
\frac{d}{dt} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix} = -\frac{i}{\hbar} \begin{bmatrix} V_{11}(t) & V_{12}(t)e^{i\omega_{12}t} \\ V_{21}(t)e^{i\omega_{21}t} & V_{22}(t) \end{bmatrix} \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix} \quad (8.7)
\]
To grasp the essential features of this equation, let us introduce the following simplifying assumptions:

- $V_{11} = V_{22} = 0$. This is reasonable since $V$ is supposed to represent interaction between different states.
- $V_{12}(t) = V_{21}(t) = v$ (constant) This may appear to contradict with the current theme of time-dependent interaction. The idea will be clarified later in the Question.
- $\omega_{12} = 0$, namely, $E_1^{(0)} = E_2^{(0)}$, so the two states are in “resonance”.

These simplify Eq (8.7)
\[
\frac{d}{dt} c_1 = -\frac{i}{\hbar} v c_2, \quad \frac{d}{dt} c_2 = -\frac{i}{\hbar} v c_1 \quad (8.8)
\]
For the initial condition consider $c_1(0) = 1$ and $c_2(0) = 0$. This means that the system population starts from state 1 and then transfers to state 2 due to the interaction. With this initial condition, the solution of Eq (8.8) is given by
\[
c_1(t) = \cos(vt/\hbar), \quad c_2(t) = i \sin(vt/\hbar) \quad (8.9)
\]
Therefore, $c_1$ and $c_2$ show alternate oscillation with the period $\propto \nu^{-1}$, which we call “resonance” between the two states.

Note that the larger interaction $\nu$ results in faster resonance.

**Question**

1. Derive Eq (8.9) from Eq (8.8). It is useful to consider $c_1 + c_2$ and $c_1 - c_2$.

2. Consider time-dependent interaction $V_{12}(t) = \nu e^{-i\omega t}$ and $V_{21}(t) = \nu e^{i\omega t}$. (This implies that $V(t)$ is Hermite, $V_{12}(t) = V_{21}(t)^\ast$.) Assume again $V_{11} = V_{22} = 0$, but this time $\omega_{12} \neq 0$, i.e., the two states have different energies $E_1^{(0)} \neq E_2^{(0)}$ (off-resonant). Now, what happens if the frequency $\omega$ of the interaction coincides with the energy gap $\omega_{12}$? What is the implication of this to spectroscopies?

**8.3 Perturbation theory**

As shown in Eq (8.7) for the $2 \times 2$ case, Eq (8.6) may be written in a matrix form

$$\frac{d}{dt} c(t) = -\frac{i}{\hbar} W(t) \cdot c(t) \quad (8.10)$$

where the elements of the matrix $W(t)$ is given by $[W(t)]_{kn} \equiv e^{i\omega_{kn}t}V_{kn}(t)$. This can be formally integrated as

$$c(t) = c(0) - \frac{i}{\hbar} \int_0^t W(\tau) \cdot c(\tau) d\tau \quad (8.11)$$

This does not solve the problem since the right-hand-side contains $c(t)$ itself in the integral. However, a recursive expansion obtained from this may be instructive. Inserting the whole right hand side of Eq (8.11) into $c(\tau)$ in the integral

$$c(t) = c(0) - \frac{i}{\hbar} \int_0^t W(\tau) \cdot \left\{ c(0) - \frac{i}{\hbar} \int_0^\tau W(\tau') \cdot c(\tau') d\tau' \right\} d\tau$$

$$= c(0) - \frac{i}{\hbar} \int_0^t W(\tau) \cdot c(0) d\tau + \left( \frac{-i}{\hbar} \right)^2 \int_0^t d\tau \int_0^\tau d\tau' W(\tau) \cdot W(\tau') \cdot c(\tau')$$

$$= c(0) - \frac{i}{\hbar} \int_0^t W(\tau) \cdot c(0) d\tau + \left( \frac{-i}{\hbar} \right)^2 \int_0^t d\tau \int_0^\tau d\tau' W(\tau) \cdot W(\tau') \cdot c(\tau')$$

$$\quad (8.12)$$
If we do this replacement again for the rightmost \( c(\tau') \), a term of order \( W^3 \) will emerge. By repeating this, we obtain the perturbation expansion in terms of the interaction \( W \).

The first-order perturbation formula is simple and useful in many cases

\[
\mathbf{c}^{(1)}(t) = \mathbf{c}(0) - \frac{i}{\hbar} \int_0^t \! d\tau \mathbf{W}(\tau) \cdot \mathbf{c}(0)
\]  

(8.13)

Here the two state example would be illustrative again.

\[
\begin{bmatrix} c_1^{(1)}(t) \\ c_2^{(1)}(t) \end{bmatrix} = \begin{bmatrix} c_1(0) \\ c_2(0) \end{bmatrix} - \frac{i}{\hbar} \int_0^t \! d\tau \begin{bmatrix} V_{11}(\tau) & e^{i\omega_{12}\tau} V_{12}(\tau) \\ e^{i\omega_{21}\tau} V_{21}(\tau) & V_{22}(\tau) \end{bmatrix} \begin{bmatrix} c_1(0) \\ c_2(0) \end{bmatrix}
\]  

(8.14)

As before, let us consider the initial condition where the system start in state 1, i.e., \( c_1(0) = 1 \) and \( c_2(0) = 0 \). The population in state 2 will grow along time due to the interaction. From Eq (8.14)

\[
c_2^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \! d\tau V_{21}(\tau) e^{i\omega_{21}\tau}
\]  

(8.15)

The population in state 2 is

\[
P_2^{(1)}(t) = |c_2^{(1)}(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t \! d\tau V_{21}(\tau) e^{i\omega_{21}\tau} \right|^2
\]  

(8.16)

### 8.4 Fermi’s golden rule

The integration of Eq (8.16) is easy when \( V_{21} \) does not depend on time. We get

\[
P_2^{(1)}(t) = |V_{21}|^2 \frac{\sin^2(\omega_{21}t/2)}{(\hbar\omega_{21}/2)^2}
\]  

(8.17)

**Question:** Derive Eq (8.17). How does this look like as a function of \( \omega_{21} \)?

Equation (8.17) as a function of \( \omega_{21} \) has a peak at \( \omega_{12} = 0 \) whose width and height are proportional to \( \hbar/t \) and \( (t/\hbar)^2 \), respectively. Thus, it becomes sharper and sharper as time \( t \) increases. \( \omega_{12} = 0 \) means \( E_2^{(0)} = E_1^{(0)} \), thus the transition probability is largest when the energy is conserved. This condition of energy conservation becomes more and more strict as \( t \) increases. In other words, the energy conservation is less strict in the shorter time. This is a manifest of the uncertainty principle between time and energy.
In the limit of \( t \to \infty \), Eq. (8.17) is written (symbolically) by using the so-called delta-function
\[
P^{(1)}_2(t) \to |V_{21}|^2 \frac{2\pi t}{\hbar} \delta(E^{(0)}_2 - E^{(0)}_1) \tag{8.18}
\]
(You don’t need to worry too much about the mathematical issues around the delta-function. It suffices here to consider it as a sharp limit of Eq. (8.17)). The right hand side is proportional to \( t \), whose coefficient gives the transition rate
\[
k_{21} = \frac{2\pi}{\hbar} |V_{21}|^2 \delta(E^{(0)}_2 - E^{(0)}_1) \tag{8.19}
\]
This is called Fermi’s golden rule.

### 8.5 First-order spectra

As its name implies, the golden rule can be applied to a number of different phenomena. The most important in chemistry is to absorption and emission spectra. Remember the dipole approximation of the interaction between the molecules and the electric field, Eq. (7.8) of Sec 7. By replacing the static field \( \epsilon \) by an oscillating one, \( \epsilon e^{\pm i\omega t} \), we obtain the dipole approximation of the light-molecule interaction

\[
V(t) = -\mu \epsilon e^{\pm i\omega t} \tag{8.20}
\]

Then, in Eq. (8.16), the matrix element \( V_{21} \) is replaced by the transition dipole \( \mu_{21} = \langle 2 | \mu | 1 \rangle \) and the exponential is by \( e^{i(\omega_{21} \pm \omega)\tau} \). The Fermi’s golden rule is thus expressed as

\[
k_{21} = \frac{2\pi}{\hbar} \epsilon^2 |\mu_{21}|^2 \delta(E^{(0)}_2 - E^{(0)}_1 \pm \hbar\omega) \tag{8.21}
\]

This represents the photo-absorption and emission between the states 1 and 2.

**Question:** Suppose the state 2 is higher in energy than state 1. Which sign of \( \pm \hbar\omega \) corresponds to the absorption?

### 8.6 Franck-Condon principle

In the adiabatic (Born-Oppenheimer) approximation where the motions of electrons and nuclei are separated, the molecular wave function is represented by a product of electronic and nuclear parts

\[
\Phi_{\epsilon,\nu}(r, R) = \chi_{\epsilon,\nu}(R) \phi_{\epsilon}(r; R) \tag{8.22}
\]
where $\varepsilon$ and $\nu$ are the electronic and nuclear quantum numbers, respectively. Namely, $\varphi_\varepsilon(r; R)$ is the electronic wave function of the $\varepsilon$-th electronic state which is a function of the electronic coordinates $r$ and depends parametrically on the nuclear coordinates $R$. $\chi_{\varepsilon, \nu}(R)$ is the nuclear wave function of the $\nu$-th nuclear (vibrational or rotational) state on the adiabatic potential surface of the $\varepsilon$-th electronic state.

The electronic transitions induced by a photon absorption or emission can be represented by the change of quantum numbers $(\varepsilon, \nu) \rightarrow (\varepsilon', \nu')$. The transition dipole of this process is

$$
\mu_{\varepsilon'\nu', \varepsilon\nu} = \langle \varepsilon' \nu' | \mu | \varepsilon \nu \rangle = \int dR \int dr \chi_{\varepsilon'\nu'}(R)^* \varphi_{\varepsilon'}(r; R)^* \mu_{\varepsilon\nu}(R) \varphi_{\varepsilon}(r; R) \tag{8.23}
$$

Let us carry out the integration over the electronic coordinate $r$ first,

$$
= \int dR \chi_{\varepsilon'\nu'}(R)^* \left\{ \int dr \varphi_{\varepsilon'}(r; R)^* \mu_{\varepsilon\nu}(r; R) \right\} \chi_{\varepsilon\nu}(R) \tag{8.24}
$$

The braced integral is the electronic transition dipole which we will denote as $\mu_{\varepsilon'\varepsilon}(R)$. It generally depends on the nuclear coordinate $R$. However, to a good approximation, the dependence on $R$ may be neglected and $\mu_{\varepsilon'\varepsilon}(R)$ be represented by the value at the equilibrium nuclear configuration $R_0$,

$$
\mu_{\varepsilon'\nu', \varepsilon\nu} \simeq \mu_{\varepsilon'\varepsilon}(R_0) \cdot \langle \chi_{\varepsilon'\nu'} | \chi_{\varepsilon\nu} \rangle \tag{8.25}
$$

The factor $\langle \chi_{\varepsilon'\nu'} | \chi_{\varepsilon\nu} \rangle$, given by the overlap integral between the nuclear wave functions of the initial and final states of the transition, is called the “Franck-Condon factor”.

You might remember that the conventional (or semi-classical) description of the Franck-Condon principle is stated as follows:

Because the electrons move much faster than the heavy nuclei, the nuclei don’t move during the fast electronic transitions, which is pictured on the potential energy diagrams as “vertical transitions”.

This qualitative description is made more precise by Eq (8.25).

**Question:** Sketch the potential energy curves and nuclear wave functions of the ground and first excited electronic states of a diatomic. Using this, explain why the Franck-Condon overlap is large for the vertical transitions.
Appendices

A Gaussian wave packet

If we employ a Gaussian distribution \( w(k) \propto e^{-a^2(k-k_0)^2/2} \) for the weight of superposition in Eq (3.7),

\[
\psi_{wp}(x,t) \propto \int_{-\infty}^{+\infty} e^{-a^2(k-k_0)^2/2} \psi_k(x,t) \, dk
\]  

(A.1)

This integration is slightly tedious although very straightforward. The result is

\[
\psi_{wp}(x,t) \propto \left[a(1 + \frac{i\hbar t}{ma^2})\right]^{-1/2} \exp\left[-\frac{(x - \hbar k_0 t/m)^2}{2a^2(1 + i\hbar t/ma^2)} - i k_0 x + \frac{i\hbar k_0^2 t}{2m}\right]
\]  

(A.2)

(To derive, use a well-known integration formula \( \int_{-\infty}^{+\infty} e^{-ax^2+ibx} \, dx = \sqrt{\pi} e^{-b^2/4a}. \) )

This has a simple form at \( t = 0 \)

\[
\psi_{wp}(x,0) \propto \exp\left[-\frac{x^2}{2a^2} - i k_0 x\right]
\]  

(A.3)

peaked at \( x = 0 \) and having a width of \( \simeq a \).

The probability amplitude, given by the absolute square of the wave function, also has a Gaussian form

\[
|\psi_{wp}(x,t)|^2 \propto \exp\left[-\frac{(x - \hbar k_0 t/m)^2}{a^2(1 + i\hbar t/ma^2)}\right]
\]  

(A.4)

whose peak and width depend on time as

\[
\text{Peak at } x = \frac{\hbar k_0}{m} t, \quad \text{Width } \simeq a\sqrt{1 + i\hbar t/ma^2}
\]  

(A.5)

Namely, the packet centre travels at a constant velocity \( \hbar k_0 / m \) determined by the centre of the weight function \( w(k) \). The width of the packet broadens along time \( t \).

We can confirm that the integration of this wave packet converges,

\[
\int_{-\infty}^{+\infty} |\psi_{wp}(x,t)|^2 \, dx = \text{finite}
\]  

(A.6)

In this sense, this wave packet is a physically acceptable description of free particles, in contrast with the component wave functions \( \psi_k(x,t) \). As discussed generally in Sec 3.2, \( \psi_{wp}(x,t) \) does not satisfy the time-independent Schrödinger equation.
B Effective Hamiltonian

Let us consider the matrix eigenvalue problem

\[ Hc = Ec \]  \hspace{1cm} (B.1)

where \( c \) is an \( N \)-dimensional vector and \( H \) an \( N \times N \) matrix. We divide the problem into two sub-dimensions \( N = n_A + n_B \). Namely, we pick up the first \( n_A \) elements of \( c \) to form a new vector \( c_A \). The remaining \( n_B \) elements form \( c_B \). Accordingly, \( H \) is divided into four sub-blocks. We call this procedure a “matrix partitioning”.

\[
\begin{bmatrix}
H_{AA} & H_{AB} \\
H_{BA} & H_{BB}
\end{bmatrix}
\begin{bmatrix}
c_A \\
c_B
\end{bmatrix}
= E
\begin{bmatrix}
c_A \\
c_B
\end{bmatrix}
\]  \hspace{1cm} (B.2)

Or equivalently,

\[
\begin{align*}
H_{AA}c_A + H_{AB}c_B &= Ec_A \\
H_{BA}c_A + H_{BB}c_B &= Ec_B
\end{align*}
\]  \hspace{1cm} (B.3)

We can formally eliminate \( c_B \) as follows. From the second equation,

\[ c_B = (E1_{BB} - H_{BB})^{-1}H_{BA}c_A \]  \hspace{1cm} (B.4)

By inserting this into the first equation, we obtain

\[ H^{\text{eff}}c_A = Ec_A \]  \hspace{1cm} (B.5)

where

\[ H^{\text{eff}} \equiv H_{AA} + H_{AB}(E1_{BB} - H_{BB})^{-1}H_{BA} \]  \hspace{1cm} (B.6)

In this way, the size of the matrix eigenvalue problem has been reduced from \( N \) to \( n_A \), and Eqs (B.1) and (B.6) are still equivalent. Although the size of the matrix is reduced, we have a price to pay: \( H^{\text{eff}} \) contains the unknown \( E \) which complicates the problem. Nonetheless, Eq (B.6) can be a useful starting point for various approximations. \( H^{\text{eff}} \) is called “Effective Hamiltonian”.

The variation-perturbation theory can be considered as a special case of the Effective Hamiltonian method, which is derived by

1. taking \( n_A=1 \) (i.e., \( H_{AA}=H_{11} \)),
2. approximating \( E=H_{11} \) in \( H^{\text{eff}} \), and
3. neglecting the off-diagonals in \( H_{BB} \)
Question: Confirm that the 2nd-order variation-perturbation formula Eq (6.3) of Sec 6 is obtained by the above procedure 1-3.

The generalization to the non-orthogonal basis, $S \neq I$, is straightforward. The original eigenvalue equation

$$Hc = ESc$$

is partitioned as

$$\begin{bmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = E \begin{bmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix}$$

from which the effective Hamiltonian is derived as

$$H_{\text{eff}} c_A = ES_{AA} c_A$$

$$H_{\text{eff}} = H_{AA} + (H_{AB} - ES_{AB})(ES_{BB} - H_{BB})^{-1}(H_{BA} - ES_{BA})$$

The non-orthogonal variation-perturbation theory is derived as

$$E \simeq H_{11} + \sum_{k \neq 1} \frac{|H_{1k} - S_{1k}H_{11}|^2}{H_{11} - H_{kk}} + \cdots$$

Question: Verify these.

C Frontier MO Theory

The summation $\sum_{k \in B}$ of Eq (6.11) in Sec 6 runs through all of the occupied and unoccupied MOs of molecule B. By removing the overlapping occupied-occupied region in the diagram below, Eq (6.11) can be simplified as

$$\Delta E = 2(\sum_{i \in A} \sum_{k \in B} \frac{|h'_{ik}|^2}{E_i - E_k})$$

This means that the interaction between the molecules A and B is represented by the interactions between the occupied and unoccupied MOs. For example, the first double summation represents interaction between the occupied MOs in molecule A and unoccupied MOs in molecule B. This may be further approximated by taking the smallest denominators, i.e., the HOMO-LUMO interactions to give the Frontier MO theory of Eq (6.12) in Sec 6.
D Energy change under electric field

The small change of energy $dE$ of a molecule under small change of electric field $d\epsilon$ is given by

$$dE = -\mu d\epsilon$$  \hspace{1cm} (D.13)

where $\mu$ is the molecular dipole moment. We need to note that the dipole moment $\mu$ depends on the field $\epsilon$ as in Eq (7.1). Therefore, to evaluate the net energy change $E$ under the electric field $\mathcal{E}$ we need to carry out integration

$$E(\mathcal{E}) - E(0) = - \int_{0}^{\mathcal{E}} \mu(\epsilon) \, d\epsilon$$

$$= - \int_{0}^{\mathcal{E}} (\mu + \alpha \epsilon + \frac{1}{2} \beta \epsilon^2 + \cdots) \, d\epsilon$$  \hspace{1cm} (D.14)

$$= -\mu \mathcal{E} - \frac{1}{2} \alpha \mathcal{E}^2 - \frac{1}{3!} \beta \mathcal{E}^3 + \cdots$$