

Chemistry BC3253x:
Structure, Bonding, and Spectroscopy
 aka Quantum Chemistry

B. Methods of Approximation:
Perturbation Theory
Time-dependent perturbation theory
The Variational Method

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V. Atomic structure and atomic spectra

B. Approximate Methods for many-electron systems

1. Time independent perturbation theory: first order energy correction
 application to He: comparison with independent electron result.
 atomic units for QM calculations
2. Time dependent perturbation theory: electric dipole selection rules
 If M_{if} is zero, the transition $i \rightarrow f$ is forbidden
3. The Variation method
 - a. Theorem: if Φ is an arbitrary normalized function, then $\epsilon = \geq E_0$
 - b. Application: guess a function Φ with variable parameters
 Linear combinations of known functions \rightarrow secular determinant
 - c. Calculation of structure of many-electron atoms
 self consistent field (SCF) model (Hartree and Fock, 1927-1930)

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Perturbation Theory

Wish to solve $H\psi = E\psi$, but we cannot: it is too hard.

Write $H = H^0 + H^1$ where H^1 is a small part of H

and we *can* solve the Schrodinger eqn for H^0 : $H^0\psi^0 = E^0\psi^0$

Let $\psi = \psi^0 + \Delta\psi$ and $E = E^0 + \Delta E$ **Can we find $\Delta\psi$ and ΔE ?**

Since H^1 is small, $\Delta\psi$ and ΔE are probably small corrections too.

$$H\psi = E\psi \rightarrow (H^0 + H^1)(\psi^0 + \Delta\psi) = (E^0 + \Delta E)(\psi^0 + \Delta\psi)$$

$$H^0\psi^0 + H^0\Delta\psi + H^1\psi^0 + H^1\Delta\psi = E^0\psi^0 + E^0\Delta\psi + \Delta E\psi^0 + \Delta E\Delta\psi$$

Red terms are products of two small pieces:

make the approximation that they are negligible.

$$H^0\Delta\psi + H^1\psi^0 = E^0\Delta\psi + \Delta E\psi^0$$

Multiply from left by ψ^{0*} and integrate over all variables.

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Perturbation Theory

$$H^0\Delta\psi + H^1\psi^0 = E^0\Delta\psi + \Delta E\psi^0$$

Multiply from left by ψ^{0*} and integrate over all variables

Term 1: $\int \psi^{0*} H^0 \Delta\psi \, d\tau = \int \Delta\psi H^0 \psi^{0*} \, d\tau$ since H is Hermitian

so first term = $E^0 \int \Delta\psi \psi^{0*} \, d\tau$

Term 2: $\int \psi^{0*} H^1 \psi^0 \, d\tau$

Term 3: $\int \psi^{0*} E^0 \Delta\psi \, d\tau = E^0 \int \psi^{0*} \Delta\psi \, d\tau$ equal to term 1!

Term 4: $\int \psi^{0*} \Delta E \psi^0 \, d\tau = \Delta E \int \psi^{0*} \psi^0 \, d\tau = \Delta E$

$$\text{Result: } \Delta E = \int \psi^{0*} H^1 \psi^0 \, d\tau$$

Very powerful approximate result.

First-order energy correction from zeroth-order wave functions!

we did this in the case of the magnetic field: $H^1 = -\boldsymbol{\mu} \cdot \mathbf{B}$

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Perturbation Theory: application

Applications (examples in McQuarrie):

putting small potential into particle-in-a-box

adding cubic anharmonic term to SHO [7-1]

Rigid Rotor in a small electric field (Stark Effect)

consider molecule with small electric dipole moment μ
pointing along the molecular axis r

$H^1 = -\mu \cdot E$ where E is the external electric field

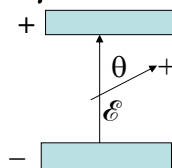
$H^1 = -\mu \mathcal{E} \cos\theta$ where \mathcal{E} is the field strength

What is ΔE for $Y_{1,0}$? $Y_{1,0} = (3/4\pi)^{1/2} \cos\theta$

$\Delta E = \int \psi^{0*} H^1 \psi^0 d\tau = -\mu \mathcal{E} (3/4\pi) \int \int \cos^3\theta \sin\theta d\theta d\phi$

but $\int_0^\pi \cos^3\theta \sin\theta d\theta = 0$

to first order, the Stark effect on RR energy levels is zero.



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Perturbation Theory: application

Rigid Rotor in a small electric field (Stark Effect)

to first order, the effect on the energy is zero.

other methods show that $E(\mathcal{E}) = E^0 - c\mathcal{E}^2$

The Stark effect is **second-order**

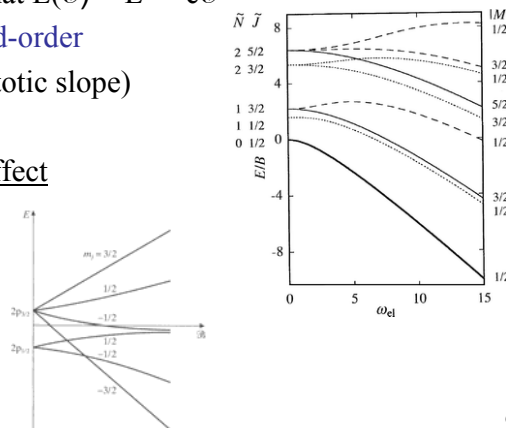
(curves have zero asymptotic slope)

Compare with Zeeman effect

ΔE is proportional to B :

a linear or

first-order effect.



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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

This topic treated near end of McQuarrie (p. 472).

Interaction of **light** (electromagnetic radiation) with **molecules**.

Light causes transitions between quantum states.

Must consider time explicitly:

light is an electric and magnetic field which oscillates in time.

$H^0(\mathbf{q})$ = exact Hamiltonian for the atom or molecule **in the dark**.

\mathbf{q} vector of all the coordinates for the problem.

Solutions to the **time-dependent Schrodinger equation**:

an orthonormal set of wavefunctions $\Psi_n^0(\mathbf{q}, t)$:

$$H^0 \Psi_n^0(\mathbf{q}, t) = i\hbar \partial \Psi_n^0 / \partial t \quad (1)$$

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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

$$H^0 \Psi_n^0(\mathbf{q}, t) = i\hbar \partial \Psi_n^0 / \partial t \quad (1)$$

Since H^0 does not involve time, we know that

$$\Psi_n^0(\mathbf{q}, t) = \psi_n^0(\mathbf{q}) e^{iE_n t/\hbar} \quad (2)$$

$\psi_n^0(\mathbf{q})$ = solutions to the time-independent Schrodinger equation:

$$H^0 \psi_n^0(\mathbf{q}) = E_n \psi_n^0(\mathbf{q}) \quad (3)$$

In the simplest picture, the **electric dipole approximation**,

light is taken to be an oscillating electric field E .

Polarized in the z direction, with frequency ω and amplitude E_z ,

$$E = E_z \cos(\omega t)$$

In the dipole approximation, this field induces a perturbation:

$$H^1 = -\mu \cdot E = -\mu_z E_z \cos(\omega t)$$

μ is the **dipole operator**, molecular property discussed later.

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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

Want to solve the Schrodinger equation for the molecule plus light:

$$\hat{H} = \mathbf{H} = \mathbf{H}^0 + \mathbf{H}^1.$$

The functions $\Psi_n^0(\mathbf{q}, t)$ form a **complete orthonormal set**.

Use to expand the unknown solution to the combined problem:

$$\Psi(\mathbf{q}, t) = \sum_k c_k(t) \Psi_k^0(\mathbf{q}, t) \quad (4)$$

$c_k(t)$ = amplitude ($c_k^* c_k$ = probability) that molecule is in state k

Note that $c_k(t)$ can change as time progresses.

Substitute into the time-dependent Schrödinger equation:

$$\hat{H}\Psi = \sum_k c_k \hat{H}^0 \Psi_k^0 + \sum_k c_k \hat{H}^1 \Psi_k^0 = i\hbar \frac{\partial \Psi}{\partial t} = i\hbar \sum_k c_k \frac{\partial \Psi_k^0}{\partial t} + i\hbar \sum_k \frac{\partial c_k}{\partial t} \Psi_k^0$$

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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

$$\hat{H}\Psi = \sum_k c_k \hat{H}^0 \Psi_k^0 + \sum_k c_k \hat{H}^1 \Psi_k^0 = i\hbar \frac{\partial \Psi}{\partial t} = i\hbar \sum_k c_k \frac{\partial \Psi_k^0}{\partial t} + i\hbar \sum_k \frac{\partial c_k}{\partial t} \Psi_k^0$$

Multiply from left by Ψ_j^{0*} , integrate $d\tau$ (c's depend on t only):

$$\sum_k c_k \int \Psi_j^0 * \hat{H}^0 \Psi_k^0 d\tau + \sum_k c_k \int \Psi_j^0 * \hat{H}^1 \Psi_k^0 d\tau = i\hbar \sum_k c_k \int \Psi_j^0 * \frac{\partial \Psi_k^0}{\partial t} d\tau + i\hbar \sum_k \frac{\partial c_k}{\partial t} \int \Psi_j^0 * \Psi_k^0 d\tau$$

Based on equation (1), first terms on either side cancel.

Orthogonality simplifies last term, picking out the jth term only:

$$i\hbar \frac{\partial c_j}{\partial t} = \sum_k c_k \int \Psi_j^0 * \hat{H}^1 \Psi_k^0 d\tau \quad (5)$$

The rate of increase in amplitude of the jth state depends on how the perturbation term \hat{H}^1 couples state j to the other states k.

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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

(1) introduce the explicit electric dipole term and assume

(2) system starts in state k: at $t = 0$ $c_k = 1$ and all other $c_j = 0$.

$$i\hbar \frac{\partial c_j}{\partial t} = -E_z \cos(\omega t) \cdot e^{i(E_j - E_k)t/\hbar} \cdot \int \Psi_j^0 * \hat{\mu}_z \Psi_k^0 d\tau \quad (6)$$

Define M_{jk} the **transition dipole integral**: $M_{kj} = \int \Psi_j^0 * \hat{\mu}_z \Psi_k^0 d\tau$

and $\omega_0 \equiv (E_j - E_k)/\hbar$, **transition frequency** between levels j and k

$$i\hbar \frac{\partial c_j}{\partial t} = -E_z \cdot M_{jk} \cdot \cos(\omega t) \cdot e^{i\omega_0 t/\hbar} = -E_z \cdot M_{jk} \cdot [(e^{i\omega t} + e^{-i\omega t})/2] \cdot e^{i\omega_0 t/\hbar}$$

$$i\hbar \frac{\partial c_j}{\partial t} = -\frac{1}{2} E_z \cdot M_{jk} \cdot [e^{i(\omega_0 + \omega)t} + e^{i(\omega_0 - \omega)t}] \quad (7)$$

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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

$$i\hbar \frac{\partial c_j}{\partial t} = -\frac{1}{2} E_z \cdot M_{jk} \cdot [e^{i(\omega_0 + \omega)t} + e^{i(\omega_0 - \omega)t}] \quad (7)$$

a first order differential equation for $c_j(t)$.

Integrate for small t:

$$c_j(t) = \frac{E_z M_{jk}}{2\hbar} \left\{ \frac{e^{i(\omega_0 + \omega)t} - 1}{(\omega_0 + \omega)} + \frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)} \right\} \quad (8)$$

equation involves two frequencies: ω , the frequency of the light, and ω_0 , the frequency corresponding to the k to j transition.

Numerators small. ω values typically 10^{12} to 10^{15} s⁻¹, so

denominators huge unless $\omega \approx \pm \omega_0$

Conclusion: transitions occur when light frequency in **resonance**.

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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

$$c_j(t) = \frac{E_z M_{jk}}{2\hbar} \left\{ \frac{e^{i(\omega_0 + \omega)t} - 1}{(\omega_0 + \omega)} + \frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)} \right\} \quad (8)$$

$\omega \approx +\omega_0$ is absorption, $\omega \approx -\omega_0$ emission of light.

Absorption and **stimulated emission** terms. (LASERS)

Expand the exponential [$e^x = 1 + x + (\text{higher terms negligible})$]

$$|c_j| = \frac{E_z M_{jk}}{2\hbar} t \quad \longrightarrow \quad c_j^2 = \frac{E_z^2 M_{jk}^2}{4\hbar^2} t^2$$

Conclusions: transition probability from k to j

(1) proportional to E^2 (intensity of light)

(2) proportional to M_{jk}^2 .

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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

Transition probability from k to j proportional to M_{jk}^2 .

Often we can show that for certain states, $M_{jk} = 0$.

Those transitions are **electric dipole forbidden**.

Electric **dipole selection rules** tell you which transitions will be absent (or very weak) in the observed spectrum.

Calculated from wave functions of the molecule in the dark.

Example: spectrum of H atom.

dipole operator is $\boldsymbol{\mu} = e \mathbf{r}$ (r vector points to electron)

Evaluate separately the x, y, z components of M_{jk}

to find selection rules for light polarized along (x, y, or z):

$M_{jk}(x) = e \int \psi_j^* x \psi_k d\tau$, $M_{jk}(y) = e \int \psi_j^* y \psi_k d\tau$, etc.

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Time Dependent Perturbation Theory and Electric Dipole Selection Rules

Find the x, y, z components of M_{jk} : $M_{jk}(x) = e \int \psi_j^* x \psi_k d\tau \dots$
if all are zero, transition forbidden.

In principal, complicated multidimensional integrals,
but symmetry can often be used to simplify.

Results:

For H atom: $\Delta n = \text{anything}$; $\Delta \ell = \pm 1$, $\Delta m = 0, \pm 1$, $\Delta m_s = 0$

For SHO: $\Delta v = \pm 1$ (fundamental transition)

For RR: $\Delta J = \pm 1$, $\Delta m_j = 0, \pm 1$.

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Getting ready for many electron atoms: atomic units

Constants m_e , \hbar , $(4\pi\epsilon_0)$, e in many equations.

Values available in SI units.

But we can choose a set of units that makes **each of these = 1!**

How? Measure mass in units of m_e , charge in units of e ,

angular momentum in units of \hbar , permittivity in units of $(4\pi\epsilon_0)$

Previously we defined $a_0 = \text{Bohr radius}$, unit of length

$a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$. But in these units, $a_0 = 1$.

Also $E_h = \text{Hartree} = m_e e^4 / (4\pi\epsilon_0)^2 \hbar^2$ is also equal to 1.

McQuarrie, Table 8-1, lists other derived atomic units.

These make the equations in QM look much simpler

(but sometimes confusing because constants are hidden)

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atomic units

Hamiltonian for H atom

in arbitrary units: $\hat{H} = (-\hbar^2/2m_e)\nabla^2 - Ze^2/(4\pi\epsilon_0) r$

in atomic units: $\hat{H} = -1/2\nabla^2 - Z/r$

Energy levels for H atom

in arbitrary units: $E_n = -m_e Z^2 e^4 / 2(4\pi\epsilon_0)^2 \hbar^2 n^2$

in atomic units: $E_n = -Z^2 / 2n^2$

Ground state wavefunction for H atom:

in arbitrary units: $\psi_0 = 2 (Z/a_0)^{3/2} (1/4\pi)^{1/2} e^{-Zr/2a_0}$

in atomic units: $\psi_0 = (Z^3/\pi)^{1/2} e^{-Zr/2}$

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He atom: Hamiltonian in atomic units

Hamiltonian for **He atom** (nucleus charge Z + two electrons 1, 2)

in arbitrary units:

$$\hat{H} = (-\hbar^2/2m_e)(\nabla_1^2 + \nabla_2^2) + (e^2/4\pi\epsilon_0) \{-Z/r_1 - Z/r_2 + 1/r_{12}\}$$

in atomic units:

$$\hat{H} = (-1/2)(\nabla_1^2 + \nabla_2^2) + \{-Z/r_1 - Z/r_2 + 1/r_{12}\}$$

Kinetic energy term for each electron,

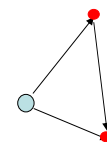
(approximation that the nucleus is fixed, since so much heavier)

plus three electrostatic potential energy terms:

nucleus and electron 1 (instantaneous separation r_1),

nucleus and electron 2 (instantaneous separation r_2),

electron 1 and electron 2 (distance r_{12}).



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He atom: solving the Schrodinger equation

Schrodinger equation in atomic units:

$$\hat{H}\psi = \{-1/2\nabla_1^2 - 1/2\nabla_2^2 + -Z/r_1 - Z/r_2 + 1/r_{12}\} \psi = E\psi$$

Use spherical polar coordinates for \mathbf{r}_1 and \mathbf{r}_2

r_{12} is a complicated function of these.

What if we ignored the electron-electron repulsion?

Then $\hat{H} = \hat{H}_1 + \hat{H}_2$ where $\hat{H}_k = \{-1/2\nabla_k^2 - Z/r_k\}$

We know the eigenvalues of each \hat{H}_k : H atom functions!

Hypothesis: suppose $\psi = \psi_1\psi_2$ If solution is a product, then

$$\hat{H}\psi = (\hat{H}_1 + \hat{H}_2)\psi_1\psi_2 = E_1\psi_1\psi_2 + E_2\psi_1\psi_2 = E \psi_1\psi_2$$

$$E = E_1 + E_2 \text{ energy is sum.}$$

This is a general result: when Ψ is a product, E is the sum.

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He atom: solving the Schrodinger equation

Ignore electron-electron repulsion ("independent electron model")

$$E_0 \text{ for He} = 2(-1/2Z^2) = -Z^2 \text{ Hartree} = -4(27.6 \text{ eV}) = \mathbf{-108 \text{ eV}}$$

Experimentally, total energy to ionize He = $IP_1 + IP_2 = 79 \text{ eV}$,

so **experimental $E_0 = -79 \text{ eV}$**

Approximation is very bad! Cannot ignore e-e repulsion.

Try perturbation theory. What is ΔE for $\hat{H}^1 = +1/r_{12}$

$$\psi_0 = \psi_1\psi_2 \quad \psi_k = (Z^3/\pi)^{1/2} e^{-Zr_k/2}$$

$$\text{So with } Z = 2, \quad \psi_0 = (8/\pi) e^{-r_1} e^{-r_2}$$

Answer (see handout) $\Delta E = 5Z/8$ in atomic units.

This gives first order energy $E_0 = E^0 + \Delta E = \mathbf{-74.8 \text{ eV}}$

Far from perfect, but a whole lot better.

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He atom: other methods of solution

Experimentally, $E_0 = -79 \text{ eV}$

First order perturbation theory: -74.8 eV

Still a large difference: why?

Independent electron model gave $E = -Z^2$.

But sometimes electron #1 close to nucleus, #2 far away.

#1 shields the interaction, so nuclear charge effectively smaller.

So each electron feels a Z_{eff} which ranges between 1 and 2.

What is average Z_{eff} ?

use equation $E = -Z^2$ with experimental $E \rightarrow Z_{\text{eff}} \sim 1.707$

but not predictive. Could we determine Z_{eff} to calculate E ?

Introduce **variational method**.

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Variational method

Theorem: if ϕ is an arbitrary normalized function, then the expectation value of the Hamiltonian operator \hat{H} calculated with ϕ is greater than or equal to the smallest eigenvalue of \hat{H} .

Symbolically: If $\epsilon = \int \phi^* \hat{H} \phi \, d\tau$, then $\epsilon \geq E_0$

Proof on next slide.

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Variational theorem

If ϕ is an arbitrary normalized function, then the expectation value of the Hamiltonian operator \hat{H} calculated with ϕ is greater than or equal to the smallest eigenvalue of \hat{H} .

symbolically: if $\epsilon = \int \phi^* \hat{H} \phi \, d\tau$, then $\epsilon \geq E_0$

Let $\phi = \sum c_k \psi_k$ where $\{\psi_k\}$ is a complete orthonormal set.

$$\begin{aligned} \epsilon &= \int \sum_k c_k^* \psi_k^* \hat{H} \sum_j c_j \psi_j \, d\tau = \int \sum_k c_k^* \psi_k^* \sum_j c_j E_j \psi_j \, d\tau \\ &= \sum_k c_k^* \sum_j c_j E_j \int \psi_k^* \psi_j \, d\tau = \sum_k c_k^* \sum_j c_j E_j \delta_{kj} = \sum_k c_k^* c_k E_k \end{aligned}$$

ϕ is normalized, so $\sum c_k^* c_k = 1$. Multiply by E_0 : $E_0 = \sum E_0 c_k^* c_k$

subtract from above: $(\epsilon - E_0) = \sum (E_k - E_0) c_k^* c_k$

but $E_k - E_0 \geq 0$ and $c_k^* c_k \geq 0$ so $(\epsilon - E_0) \geq 0$; $\epsilon \geq E_0$

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Variational method

Theorem: if ϕ is an arbitrary normalized function, then the expectation value of the Hamiltonian operator \hat{H} calculated with ϕ is greater than or equal to the smallest eigenvalue of \hat{H} .

ϕ is *any* normalized function. If by great good luck,

it happens to be the ground state eigenfunction ψ_0 ,

the $\epsilon = E_0$ (also $c_0=1$ and all other $c_k=0$).

But in general, $\epsilon > E_0$

So we guess trial functions! The best guess gives the smallest E .

Include parameters: vary them to give the smallest E .

If the function is quite flexible, this can give an excellent result.

This is the **variational method**, widely used to solve the S. eqn.

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Variational method: examples

Some examples (without detailed solutions)

Example 1: Particle in box: trial function $\varphi(x) = L x(x-1)$
 problem 4.7: Gives ε 1.3% larger than exact E_1 .

Example 2: H atom. Trial wavefunction: $\varphi(r) = A e^{-\alpha r^2}$
 (we know that the correct answer is $\sim e^{-ar}$, so not exactly right)
 Answer: $\varepsilon = -0.424$ Hartrees $>$ correct value $E = -0.5$ hartrees

Example 3: SHO. Trial wavefunction: $\varphi(x) = A \cos(\lambda x)$
 in interval $(-\pi/2\lambda < x < \pi/2\lambda)$. Treat λ as variable parameter.
 Gives $\varepsilon = \frac{1}{2}\hbar\omega$ (1.14) i.e. 14% too big.

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Variational method: the He atom

Trial function $\Psi = \phi_1\phi_2$ where $\phi_k = (Z_e^3/\pi)^{1/2} e^{-Z_e r_k/2}$

ϕ_k is a H-atom like 1s function, treating Z_e as a parameter
 the Z 's in \hat{H} are the actual nuclear charges, not Z_e , so

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{Z}{r_1} - \frac{\nabla_2^2}{2} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad \text{the } Z\text{'s in } \hat{H} \text{ are the actual nuclear charges, not } Z_e, \text{ so}$$

$$\hat{H} = \left\{ -\frac{\nabla_1^2}{2} - \frac{Z_e}{r_1} \right\} + \left\{ -\frac{\nabla_2^2}{2} - \frac{Z_e}{r_2} \right\} + \frac{1}{r_{12}} + \left\{ -\frac{Z-Z_e}{r_1} - \frac{Z-Z_e}{r_2} \right\} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} + \hat{H}'$$

ϕ_k is an eigenfunction of \hat{H}_k with eigenvalue $E_k = -Z_e^2/2$

$$\hat{H}\Psi = \hat{H}_1\phi_1\phi_2 + \hat{H}_2\phi_1\phi_2 + \hat{H}_{12}\phi_1\phi_2 + \hat{H}'\phi_1\phi_2 = (E_1 + E_2)\phi_1\phi_2 + \hat{H}_{12}\phi_1\phi_2 + \hat{H}'\phi_1\phi_2$$

$$\varepsilon = \int \Psi^* \hat{H}\Psi d\tau = E_1 + E_2 + \int \phi_1\phi_2 \hat{H}_{12} \phi_1\phi_2 d\tau + \int \phi_1\phi_2 \hat{H}' \phi_1\phi_2 d\tau$$

We did the first integral in perturbation theory: it is equal to $-5Z_e/8$.

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Variational method: the He atom

The second integral requires some work:

$$\int \phi_1\phi_2 \hat{H}' \phi_1\phi_2 d\tau = -(Z - Z_e) \int \phi_1\phi_2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \phi_1\phi_2 d\tau = -(Z - Z_e) \left\{ \int \frac{\phi_1^2 \phi_2^2}{r_1} d\tau + \int \frac{\phi_1^2 \phi_2^2}{r_2} d\tau \right\}$$

The two integrals in the brackets are equivalent: focus on either:

$$\int \frac{\phi_1^2 \phi_2^2}{r_1} d\tau = \int \frac{\phi_1^2}{r_1} d\tau_1 \int \phi_2^2 d\tau_2 = \int \frac{\phi_1^2}{r_1} d\tau_1 = \frac{Z_e^3}{\pi} \int_0^\infty e^{-2Z_e r_1} r_1 dr_1 \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi$$

$$\text{The angular integrals give } 4\pi, \text{ so } \int \frac{\phi_1^2 \phi_2^2}{r_1} d\tau = 4Z_e^3 \int_0^\infty e^{-2Z_e r_1} r_1 dr_1 = \frac{4Z_e^3}{(2Z_e)^2} = Z_e$$

$$\text{Substituting: } \int \phi_1\phi_2 \hat{H}' \phi_1\phi_2 d\tau = -2(Z - Z_e)Z_e$$

$$\varepsilon = E_1 + E_2 - \frac{5Z_e}{8} - 2Z_e(Z - Z_e) = -Z_e^2 - \frac{5Z_e}{8} - 2Z_e Z + 2Z_e^2 = Z_e^2 - Z_e(2Z - \frac{5}{8})$$

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Variational method: the He atom

Therefore $\varepsilon = \int (\phi_1\phi_2) \hat{H} (\phi_1\phi_2) d\tau = Z_e^2 - Z_e(2Z - 5/8)$

Z_e is a parameter, Z is the actual nuclear charge (2 for He).

What Z_e give the smallest possible ε ?

$$d\varepsilon/dZ_e = 2Z_e - (2Z - 5/8) = 0 \rightarrow Z_e = Z - 5/16$$

For He, this gives $Z_e = 27/16 = 1.6875$, a reasonable answer:

the electron experiences an average shielded charge < 2 .

$$\varepsilon = Z_e^2 - Z_e(2Z - 5/8) = (Z - 5/16)^2 - 2(Z - 5/16)^2$$

$$= -(Z - 5/16)^2 = Z_e^2. \text{ For He, this is } -2.848 \text{ Hartrees.}$$

Experimentally, $E_0 = -79$ eV

First order perturbation theory: -74.8 eV

This variational result: -77.49 eV

Adding more parameters can give a better and better result!

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Variational method: linear combination

One very common implementation of variational method:
trial function ψ is a **linear combination** of known functions

these need not be orthogonal or normalized

$$\psi' = c_1\phi_1 + c_2\phi_2 + (\text{more terms as needed})$$

ϕ_k not eigenfunctions of the problem --- don't know these ---
but often eigenfunctions of a related problem.

ψ' is not normalized. But we can normalize it:

$$\text{if } D \equiv \int \psi'^* \psi' d\tau, \text{ then } \psi = \psi' / D^{1/2} \text{ gives normalized } \psi$$

Use the variational theorem with the normalized ψ :

$$\varepsilon = \int \psi^* \hat{H} \psi d\tau = \left(\int \psi'^* \hat{H} \psi' d\tau \right) / \left(\int \psi'^* \psi' d\tau \right)$$

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Variational method

$$\psi' = c_1\phi_1 + c_2\phi_2 \quad c_k \text{'s are constants, to be determined}$$

$$\varepsilon = \left(\int \psi'^* \hat{H} \psi' d\tau \right) / \left(\int \psi'^* \psi' d\tau \right) = N/D$$

Numerator N:

$$\begin{aligned} N &= \int \psi'^* \hat{H} \psi' d\tau = \int (c_1^* \phi_1^* + c_2^* \phi_2^*) \hat{H} (c_1 \phi_1 + c_2 \phi_2) d\tau \\ &= c_1^* c_1 \int \phi_1^* \hat{H} \phi_1 d\tau + c_1^* c_2 \int \phi_1^* \hat{H} \phi_2 d\tau \\ &\quad + c_2^* c_1 \int \phi_2^* \hat{H} \phi_1 d\tau + c_2^* c_2 \int \phi_2^* \hat{H} \phi_2 d\tau \end{aligned}$$

Define $H_{jk} \equiv \int \phi_j^* \hat{H} \phi_k d\tau$ then

$$N = c_1^* c_1 H_{11} + c_1^* c_2 H_{12} + c_2^* c_1 H_{21} + c_2^* c_2 H_{22}$$

Denominator D: $D = \int \psi'^* \psi' d\tau = \int (c_1^* \phi_1^* + c_2^* \phi_2^*) (c_1 \phi_1 + c_2 \phi_2) d\tau$

$$= c_1^* c_1 \int \phi_1^* \phi_1 d\tau + c_1^* c_2 \int \phi_1^* \phi_2 d\tau + c_2^* c_1 \int \phi_2^* \phi_1 d\tau + c_2^* c_2 \int \phi_2^* \phi_2 d\tau$$

Define $S_{jk} \equiv \int \phi_j^* \phi_k d\tau$ (called an "overlap integral") then

$$D = c_1^* c_1 S_{11} + c_1^* c_2 S_{12} + c_2^* c_1 S_{21} + c_2^* c_2 S_{22}$$

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Variational method

$$\begin{aligned} \varepsilon &= \left(\int \psi'^* \hat{H} \psi' d\tau \right) / \left(\int \psi'^* \psi' d\tau \right) \\ &= \left(c_1^* c_1 H_{11} + c_1^* c_2 H_{12} + c_2^* c_1 H_{21} + c_2^* c_2 H_{22} \right) / \\ &\quad \left(c_1^* c_1 S_{11} + c_1^* c_2 S_{12} + c_2^* c_1 S_{21} + c_2^* c_2 S_{22} \right) \end{aligned}$$

If the ϕ_k happen to be orthonormal, then $S_{jk} = \delta_{jk}$

What is the physical meaning of the H_{jk} terms? $H_{jk} \equiv \int \phi_j^* \hat{H} \phi_k d\tau$

If the functions ϕ_k were eigenfunctions of H , then

H_{jj} would be the energy E_j and

H_{jk} ($j \neq k$) would be zero.

Often they are eigenfunctions of a similar system, in which case H_{jj} are *approximate* energies, and the off-diagonal H_{jk} indicate how strongly these approximate functions are mixed together to give the true eigenfunctions of the system.

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Variational method

We want to find c_1 and c_2 that make ε a minimum.

Take $d\varepsilon/dc_1$ and $d\varepsilon/dc_2$ and set them equal to zero.

Observe that if $\varepsilon = N/D$, then $d\varepsilon/dc_k = (dN/dc_k - \varepsilon dD/dc_k)/D$

$$d\varepsilon/dc_1^* = \{c_1 H_{11} + c_2 H_{12} - \varepsilon (c_1 S_{11} + c_2 S_{12})\} / D = 0$$

$$d\varepsilon/dc_2^* = \{c_2 H_{12} + c_2 H_{22} - \varepsilon (c_2 S_{12} + c_2 S_{22})\} / D = 0$$

So

$$c_1 H_{11} + c_2 H_{12} - \varepsilon (c_1 S_{11} + c_2 S_{12}) = 0$$

$$c_2 H_{12} + c_2 H_{22} - \varepsilon (c_2 S_{12} + c_2 S_{22}) = 0$$

Collect terms with c_1, c_2 :

$$c_1 (H_{11} - \varepsilon S_{11}) + c_2 (H_{12} - \varepsilon S_{12}) = 0$$

$$c_1 (H_{21} - \varepsilon S_{21}) + c_2 (H_{22} - \varepsilon S_{22}) = 0$$

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Variational method

$$c_1 (H_{11} - \varepsilon S_{11}) + c_2 (H_{12} - \varepsilon S_{12}) = 0$$

$$c_1 (H_{21} - \varepsilon S_{21}) + c_2 (H_{22} - \varepsilon S_{22}) = 0$$

Two linear equations in two unknowns.

Standard problem in linear algebra. Find solution by setting the determinant of the matrix of coefficients equal to zero.

Note that each jk matrix element is $(H_{jk} - \varepsilon S_{jk})$

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

in a matrix, the first index gives the row, the second the column.

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Variational method: secular equation

The determinant of a 2 x 2 matrix: $\begin{vmatrix} a & b \\ c & d \end{vmatrix} \equiv ad - bc$

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

says $(H_{11} - \varepsilon S_{11})(H_{22} - \varepsilon S_{22}) - (H_{12} - \varepsilon S_{12})(H_{21} - \varepsilon S_{21}) = 0$

If we know H_{jk} and S_{jk} , we can solve for ε !

don't need to find the c_k 's first. Can get them later, if needed.

This can be extended to any number n of coefficients c_k ,

The determinant will involve a $n \times n$ matrix.

Such approach well suited to computers. **Secular equation**

wave formulation and matrix formulation are equivalent:

Schrodinger and Heisenberg pictures of QM.

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Variational method: secular equation

Solving $(H_{11} - \varepsilon S_{11})(H_{22} - \varepsilon S_{22}) - (H_{12} - \varepsilon S_{12})(H_{21} - \varepsilon S_{21}) = 0$

Example: suppose ϕ_k are orthonormal. Then $S_{jk} = \delta_{jk}$ and

$$(H_{11} - \varepsilon S_{11})(H_{22} - \varepsilon S_{22}) - (H_{12} - \varepsilon S_{12})(H_{21} - \varepsilon S_{21})$$

$$= (H_{11} - \varepsilon)(H_{22} - \varepsilon) - (H_{12})(H_{21}) = 0$$

Since H is Hermitian, $H_{12} = H_{21}$

Gives quadratic: $\varepsilon^2 - \varepsilon (H_{11} + H_{22}) + H_{11}H_{22} - H_{12}^2 = 0$

$$\varepsilon = \frac{1}{2} \{ (H_{11} + H_{22}) \pm [(H_{11} + H_{22})^2 - 4(H_{11}H_{22} - H_{12}^2)]^{1/2} \}$$

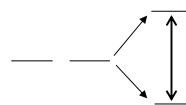
$$= \frac{1}{2} \{ (H_{11} + H_{22}) \pm [(H_{22} - H_{11})^2 + 4 H_{12}^2]^{1/2} \}$$

Application #1: suppose $H_{11} = H_{22} = E_0$

then $\varepsilon_1 = E_0 - H_{12}$ and $\varepsilon_2 = E_0 + H_{12}$

NMR: no field: both energies E_0

magnetic field induces coupling $2H_{12}$



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Variational method

we can rewrite the quadratic as

$$\varepsilon = \frac{1}{2} \{ (H_{11} + H_{22}) \pm (H_{22} - H_{11}) [1 + 4 H_{12}^2 / (H_{22} - H_{11})^2]^{1/2} \}$$

If H_{12} is small compared to the difference $H_{22} - H_{11}$

then use the series expansion for small x : $(1+x)^{1/2} = 1 + x/2 + \dots$

$$\varepsilon = \frac{1}{2} \{ (H_{11} + H_{22}) \pm (H_{22} - H_{11}) [1 + 4 H_{12}^2 / (H_{22} - H_{11})^2]^{1/2} \}$$

$$= \frac{1}{2} \{ (H_{11} + H_{22}) \pm (H_{22} - H_{11}) [1 + 2 H_{12}^2 / (H_{22} - H_{11})^2] + \dots \}$$

Taking the $-$ sign for the lower root:

$$\varepsilon_1 = \frac{1}{2} \{ (H_{11} + H_{22}) - (H_{22} - H_{11}) [1 + 2 H_{12}^2 / (H_{22} - H_{11})^2] \}$$

$$\varepsilon_1 = H_{11} - H_{12}^2 / (H_{22} - H_{11})$$

Likewise $\varepsilon_2 = H_{22} + H_{12}^2 / (H_{22} - H_{11})$

Lower state falls, upper rises, depending on magnitude of H_{12} .

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Variational method

$$\varepsilon_1 = H_{11} - H_{12}^2/(H_{22}-H_{11}) \quad \text{and} \quad \varepsilon_2 = H_{22} + H_{12}^2/(H_{22}-H_{11})$$

Suppose we partition \hat{H} as in perturbation theory: $\hat{H} = \hat{H}_0 + \hat{H}_1$

where ϕ_k are eigenfunctions of \hat{H}_0 with eigenvalues E_k^0

Just using simple perturbation theory, $\mathbf{E} = \mathbf{H}_{11}$.

Applying variational method, we do better (energy is lower):

$$\varepsilon_1 = \mathbf{H}_{11} - \mathbf{H}_{12}^2/(\mathbf{H}_{22}-\mathbf{H}_{11})$$

Observe: $H_{12} \equiv \int \phi_1^* \hat{H} \phi_2 \, d\tau = \int \phi_1^* (\hat{H}_0 + \hat{H}_1) \phi_2 \, d\tau$

$$H_{12} = \int \phi_1^* E_2^0 \phi_2 \, d\tau + \int \phi_1^* \hat{H}_1 \phi_2 \, d\tau = E_2^0 \int \phi_1^* \phi_2 \, d\tau + \int \phi_1^* \hat{H}_1 \phi_2 \, d\tau$$

$$= \int \phi_1^* \hat{H}_1 \phi_2 \, d\tau$$

orthogonality gets rid of the \hat{H}_0 term

only the perturbation \hat{H}_1 contributes to the off-diagonal term.

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Variational method: examples

This pattern of level shifts, lower level down, upper level up, when additional term added, very common.

e.g. Zeeman effect, described qualitatively earlier.

Another example: polarizability α of H atom (induces dipole μ)

$$\mu_{\text{ind}} = \alpha \mathcal{E} \quad \text{and} \quad \Delta E = -\frac{1}{2} \alpha \mathcal{E}^2$$

\hat{H}_0 = field free hamiltonian for H atom with eigenfunctions ψ^0

\hat{H}_1 = hamiltonian for added electric field \mathcal{E} along z axis = $-\mu \cdot \mathcal{E}$

Let $\Psi = c_1 \psi_{1s}^0 + c_2 \psi_{2pz}^0$

results (McQuarrie, page 272-273) $\alpha = 2.96 a_0^3/4\pi\epsilon_0$

exact result is $\alpha = 4.5 a_0^3/4\pi\epsilon_0$

ground state wavefunction picks up some $2p_z$ character

Also: put a small ramp inside the PIB (McQuarrie, p. 270 #7-4)

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Variational method: SHO + cubic

Add a small cubic term to the SHO potential (anharmonicity).

\hat{H}_0 = SHO hamiltonian with SHO eigenfunctions ϕ^0

\hat{H}_1 = hamiltonian for added cubic = $V'(x) = \gamma x^3/6$ [$\gamma = d^3V/dx^3$]

Use reduced units of SHO problem:

$$\xi = \alpha^{1/2} x \quad \text{where} \quad \alpha = \mu\omega/\hbar$$

$$\hat{H}_1 = \gamma x^3/6 = \gamma \xi^3/6\alpha^{3/2} = b\xi^3 \quad \text{where} \quad b = \gamma/6\alpha^{3/2}$$

$$\psi = c_0\phi_0 + c_1\phi_1 \quad \text{where} \quad \phi_0 = \pi^{-1/4} e^{-\frac{1}{2}\xi^2} \quad \text{and} \quad \phi_1 = (4\pi)^{-1/4} 2\xi e^{-\frac{1}{2}\xi^2}$$

Orthonormal, so $S_{ij} = \delta_{ij}$.

$$H_{00} = \int \phi_0^* \hat{H} \phi_0 \, d\tau = \int \phi_0^* (\hat{H}_0 + \hat{H}_1) \phi_0 \, d\xi = E_0 + \int \phi_0^* \hat{H}_1 \phi_0 \, d\xi$$

but ϕ_0 is even, and \hat{H}_1 is odd: integrand is odd, so integral is zero!

Likewise $H_{11} = E_1$.

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Variational method: SHO + cubic

$$H_{01} = \int \phi_0^* \hat{H} \phi_1 \, d\tau = \int \phi_0^* (\hat{H}_0 + \hat{H}_1) \phi_1 \, d\xi = E_1 \int \phi_0^* \phi_1 \, d\xi + \int \phi_0^* \hat{H}_1 \phi_1 \, d\xi$$

First term is zero: orthogonality.

$$H_{01} = \int \phi_0^* \hat{H}_1 \phi_1 \, d\xi = b \int \phi_0^* \xi^3 \phi_1 \, d\xi$$

(even)(odd)(odd): integrand is even, so *not* zero by symmetry.

$$H_{01} = b \int \phi_0^* \xi^3 \phi_1 \, d\xi = b \int (\pi^{-1/4} e^{-\frac{1}{2}\xi^2}) \xi^3 [(4\pi)^{-1/4} 2\xi e^{-\frac{1}{2}\xi^2}] \, d\xi$$

$$= 2b (2\pi)^{-1/2} \int \xi^4 e^{-\xi^2} \, d\xi \quad \text{integral from } -\infty \text{ to } +\infty$$

using integral tables, $\mathbf{H}_{01} = \mathbf{3b/8}^{1/2}$ Since Hermitian, $H_{01} = H_{10}$

Assuming that $H_{01} \ll (H_{11} - H_{00})$

$$\varepsilon_0 = H_{00} - H_{01}^2/(H_{11} - H_{00}) = E_0 - (9b^2/8)/(E_1 - E_0)$$

$$= (\frac{1}{2}\hbar\omega) - (9b^2/8\hbar\omega)$$

Anharmonicity lowers the ground state energy

Proportional to b^2 , so correction was zero as first order perturbation

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Variational method: SHO + cubic

Ground state energy with cubic term:

$$\varepsilon_0 = (\frac{1}{2}\hbar\omega) - (9b^2/4\hbar\omega) = E_0 - \Delta E_{\text{anh}}$$

with some algebra, one can show that $\Delta E_{\text{anh}} = (\hbar\omega)^2 \{\gamma^2/32k^2\}$

$$\text{So } \varepsilon_0 = (\frac{1}{2}\hbar\omega)[1 - (\hbar\omega)\{\gamma^2/16k^2\}]$$

second term dimensionless: for molecules typically about 0.01.

In IR spectroscopy, we typically write a **term expression**:

$$E_v = \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 \quad [\text{where } \omega_e \equiv \hbar\omega/hc]$$

For **HCl**, $\omega_e = 2990 \text{ cm}^{-1}$ and $\omega_e x_e = 52 \text{ cm}^{-1}$

$$E_0(\text{harmonic}) = 1495 \text{ cm}^{-1}$$

with the anharmonic term: 1482 cm^{-1} , about *1% lower*.

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Variational method: SHO + cubic

For **HCl**, experimentally $\omega_e = 2989.7 \text{ cm}^{-1}$ and $\omega_e x_e = 52.05 \text{ cm}^{-1}$

$$E_0(\text{harmonic}) = 1495 \text{ cm}^{-1}$$

$$E_0(\text{incl. cubic}) = 1482 \text{ cm}^{-1}$$

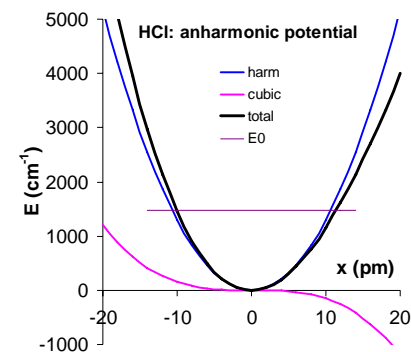
Spreadsheet anharmonic.xls

find k and γ from ω_e , $\omega_e x_e$

masses, and constants

Plot $V(x)$:

harmonic, cubic, total
note that the cubic contribution
is quite small at
the ground state energy E_0



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