

Quantum Chemistry

Lecture 11

Approximate Methods
Perturbation Theory
The Variational Principle

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Approximate Methods

The major distinction in approximate quantum theory is between perturbation theory and the variational principle. These two methods of approximation are complementary and are used both separately and in combination to solve the most complex problems.

The philosophy of the variational principle is to use the derivative of the energy with respect to a parameter in an approximate wave function. Such parameters are known as variational parameters.

Examples include the magnitude of the exponent (usually called ζ) in a modified (screened) exponential function . The coefficients of molecular orbitals are also variational parameters.

Overview of Perturbation Theory

Perturbation theory is based on the idea that a systematic modification of wave functions and energies is possible using a prescription that can be different orders.

We can speak of first order, second order and higher order perturbation theory, up to infinite order. The philosophy of this method is based on the idea that there are stages of correction possible based on an expansion of the wave function in powers of a variational parameter, usually called λ .

Perturbation Theory

We will be interested in the effect on molecules of weak interactions such as electric or magnetic fields. Moreover, Almost any process that is considered forbidden in quantum mechanics can be observed due to some higher order effect. In all of these cases we treat the effect of a small perturbation on the system using Perturbation Theory.

The hamiltonian $H^{(0)}$ is modified by a perturbative term $H^{(1)}$:

$$H^{(0)} + \lambda H^{(1)}$$

We assume that we know the zero-order (0) eigenfunctions and energies:

$$H^{(0)}\Psi_i^{(0)} = E_i^{(0)}\Psi_i^{(0)}$$

Perturbed Energy and Wave Function

The lamda, λ is just a number. It can be used to “turn on” the Perturbation. If $\lambda = 0$ then the perturbation is not present. If $\lambda = 1$ then the perturbation is present. This method is convenient so we can keep track of any changes. We can Also consider various orders or perturbation, first order, λ , second order, λ^2 etc.

$$\Psi_i = \Psi_i^{(0)} + \lambda\Psi_i^{(1)} + \lambda^2\Psi_i^{(2)} + \dots.$$

We say the $\Psi^{(1)}$ is first order correction to the wave function. Similarly, the energies can be written:

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots.$$

Convergence requires the $E^{(1)} \ll E^{(0)}$ etc.

Perturbed Energy and Wave Function

If the states are not degenerate then we find that:

$$E_i^{(1)} = \langle \Psi_i^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle$$
$$\Psi_i^{(1)} = \sum_j \frac{\langle \Psi_j^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} \Psi_j^{(0)}$$

The perturbed wave function is composed of a linear combination of terms derived from the zero-order wave function.

$$\Psi_i^{(1)} = \sum_j c_{ji} \Psi_j^{(0)}$$

The prerequisite for the existence of a perturbed wave function is that the matrix elements $\langle \Psi_j | H' | \Psi_i \rangle$ are not zero.

Starting with a general case for a perturbed Schrodinger equation:

$$H\Psi_i = E_i\Psi_i$$

We can substitute in the definitions to first order

$$(H^{(0)} + \lambda H^{(1)}) (\Psi_i^{(0)} + \lambda\Psi_i^{(1)}) = (E_i^{(0)} + \lambda E_i^{(1)}) (\Psi_i^{(0)} + \lambda\Psi_i^{(1)})$$

and expand:

$$\begin{aligned} & H^{(0)}\Psi_i^{(0)} + \lambda H^{(1)}\Psi_i^{(0)} + \lambda H^{(0)}\Psi_i^{(1)} + \lambda^2 H^{(1)}\Psi_i^{(1)} \\ &= E_i^{(0)}\Psi_i^{(0)} + \lambda E_i^{(1)}\Psi_i^{(0)} + \lambda E_i^{(0)}\Psi_i^{(1)} + \lambda^2 E_i^{(1)}\Psi_i^{(1)} \end{aligned}$$

Collecting terms in the various order $\lambda, \lambda^2, \dots$, the equation in λ is

$$H^{(0)}\Psi_i^{(1)} + H^{(1)}\Psi_i^{(0)} = E_i^{(1)}\Psi_i^{(0)} + E_i^{(0)}\Psi_i^{(1)}$$

Which we can write as

$$H^{(0)}\Psi_i^{(1)} - E_i^{(0)}\Psi_i^{(1)} = E_i^{(1)}\Psi_i^{(0)} - H^{(1)}\Psi_i^{(0)}$$

If we left-multiply by $\Psi_j^{(0)}$ we have

$$\begin{aligned}\langle \Psi_j^{(0)} | H^{(0)} | \Psi_i^{(1)} \rangle - E_i^{(0)} \langle \Psi_j^{(0)} | \Psi_i^{(1)} \rangle \\ = E_i^{(1)} \langle \Psi_j^{(0)} | \Psi_i^{(0)} \rangle - \langle \Psi_j^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle\end{aligned}$$

Where we can use the property of the Schrodinger equation solutions

$$\left(E_j^{(0)} - E_i^{(0)} \right) \langle \Psi_j^{(0)} | \Psi_i^{(1)} \rangle = E_i^{(1)} \delta_{ij} - \langle \Psi_j^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle$$

If $i = j$, then the left-hand side is zero and the first order correction in the energy can be obtained as,

$$E_i^{(1)} = \langle \Psi_i^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle$$

For $i \neq j$

$$\left(E_j^{(0)} - E_i^{(0)} \right) \langle \Psi_j^{(0)} | \Psi_i^{(1)} \rangle = - \langle \Psi_j^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle$$

To find $\Psi_i^{(1)}$ we expand in a complete set of orthonormal unperturbed wave functions.

$$\Psi_i^{(1)} = \sum_j c_{ji} \Psi_j^{(0)}$$

where

$$c_{ji} = \langle \Psi_j^{(0)} | \Psi_i^{(1)} \rangle$$

Then we can see that

$$\left(E_j^{(0)} - E_i^{(0)} \right) c_{ji} = - \langle \Psi_j^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle$$

and

$$c_{ji} = \frac{\langle \Psi_j^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}}$$

We can write down the perturbed wave function in terms of the zero order wave functions,

$$\Psi_i^{(1)} = \sum_j \frac{\langle \Psi_j^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} \Psi_j^{(0)}$$

The Anharmonic Oscillator

An example of application of perturbation theory

The energy can be written as the zero-order energy and the first order correction

$$E = E^{(0)} + \langle \Psi_i^{(0)} | H^{(1)} | \Psi_i^{(0)} \rangle$$

We must first find the zero-order wave functions. This just means we find the wave functions for the unperturbed solution to the Hamiltonian.

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} \chi + \frac{k}{2} Q^2 \chi = E \chi$$

The lowest solution is:

$$\chi_0 = \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha Q^2/2}$$

Note that the term zero-order does not mean that v must be 0.

Definition of a perturbation

Clearly we understand that in this case the zero-order Hamiltonian is

$$H^{(0)} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} + \frac{k}{2} Q^2$$

We can define the perturbation as the cubic and quartic terms
That lead to a correction of the potential energy surface

$$H^{(1)} = \frac{\beta}{6} Q^3 + \frac{\gamma}{24} Q^4$$

The first order correction to the energy is:

$$E^{(1)} = \int_{-\infty}^{\infty} \chi_0 H^{(1)} \chi_0 dQ$$

First order correction to $v = 0$

For the $v = 0$ level we have:

$$E^{(1)} = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha Q^2} \left(\frac{\beta}{6} Q^3 + \frac{\gamma}{24} Q^4\right) dQ$$

or

$$E^{(1)} = \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{\gamma}{24} \int_{-\infty}^{\infty} e^{-\alpha Q^2} Q^4 dQ$$

Which gives the correction to the energy as:

$$E^{(1)} = \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{\gamma}{24} \frac{3\pi^{1/2}}{4\alpha^{5/2}} = \frac{\gamma}{32\alpha^2}$$

First order correction to $v = 1$

For the $v = 1$ level we have:

$$E_1^{(1)} = \int_{-\infty}^{\infty} \chi_1 H^{(1)} \chi_1 dQ$$

The wave function is

$$\chi_1 = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha} Q e^{-\alpha Q^2/2}$$

And the integral we need to solve is:

$$E_1^{(1)} = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} 2\alpha Q^2 e^{-\alpha Q^2} \left(\frac{\beta}{6} Q^3 + \frac{\gamma}{24} Q^4\right) dQ$$

Once again the cubic term vanishes:

$$E_1^{(1)} = \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{2\alpha\gamma}{24} \int_{-\infty}^{\infty} e^{-\alpha Q^2} Q^6 dQ$$

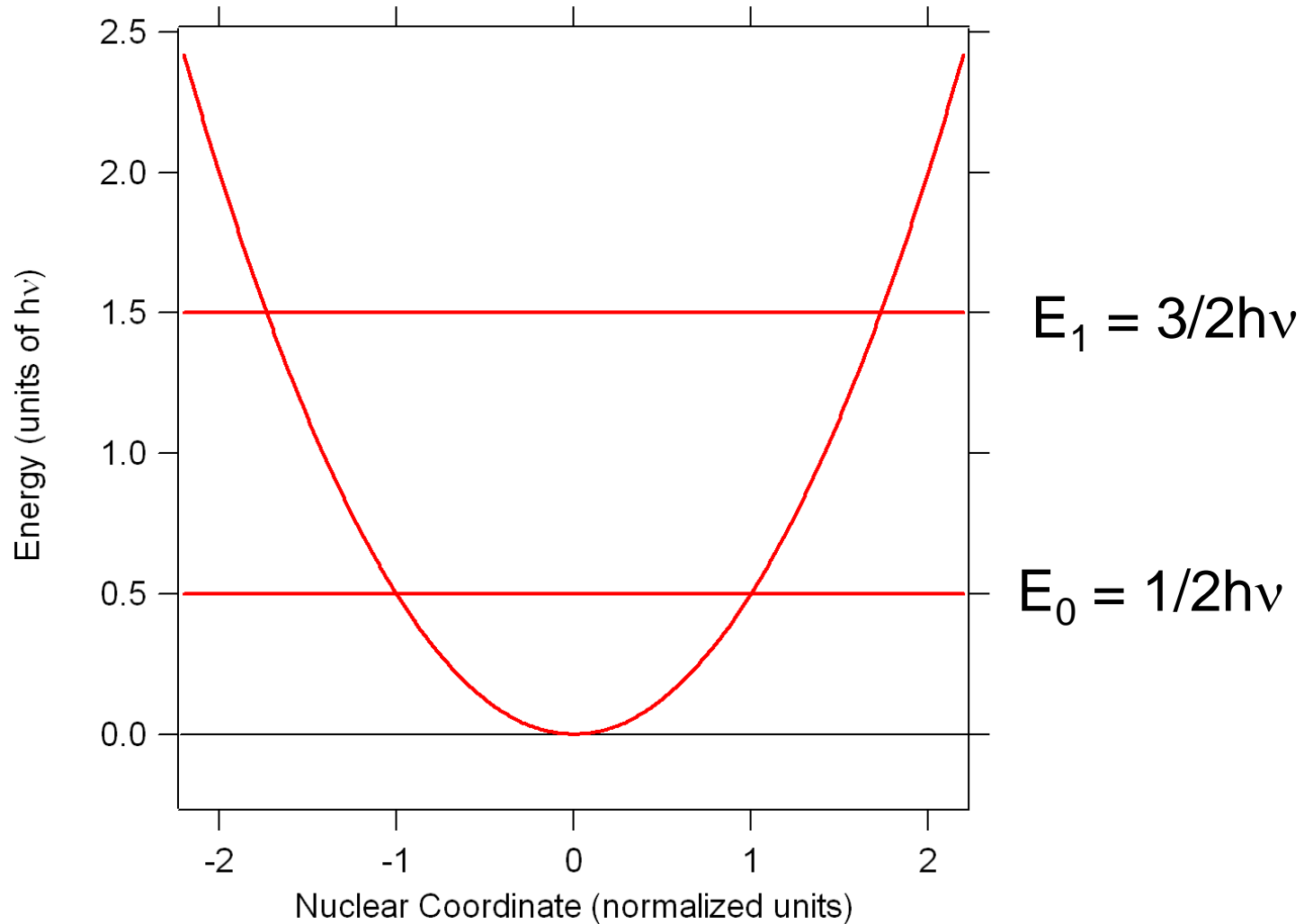
A note on perturbation order

The solution is:

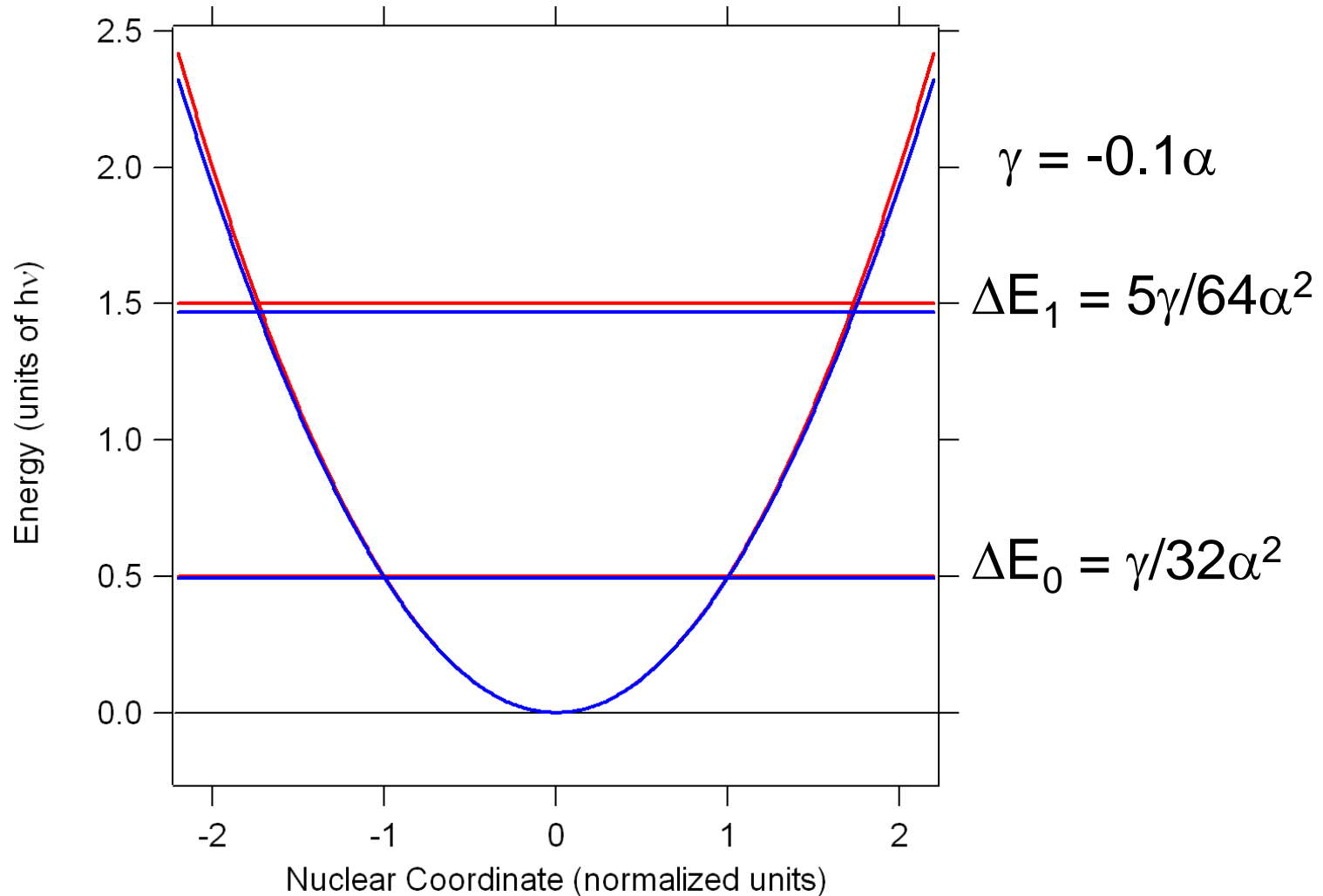
$$E_1^{(1)} = \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{\gamma}{24} \frac{15\pi^{1/2}}{8\alpha^{7/2}} = \frac{5\gamma}{64\alpha^2}$$

Note that the cubic term will always vanish to first order. This is because any vibrational wave function times itself gives an even function. The product of an even function with cubic function is odd and this integral vanishes over even limits. If we want to obtain a cubic correction, we must take perturbation theory to second order.

Zeroth Order Energies



First Order Corrections



In this example the anharmonic correction is a little more than 1%

Second Order Corrections

Second order perturbation theory is conceptually an extension of the methods used to obtain the first order correction. There are numerous instances where the second order correction is needed. For example, the first order correction may be zero. We will show a concrete example using the perturbation theory correction to the harmonic oscillator. The second order perturbation theory result is also important in calculation of magnetic superexchange, molecular polarizability and other problems that involve long-range coupling of electrons.

From this point forward the shorthand bracket notation will be used. Thus, $\Psi_n^{(0)} = |n^{(0)}\rangle$

Up to and including the second order correction, the energy is

$$E_n = E + \lambda \langle n^{(0)} | H | n^{(0)} \rangle + \lambda^2 \sum_{k \neq n} \frac{\langle k^{(0)} | H | n^{(0)} \rangle^2}{E_n^{(0)} - E_k^{(0)}} + O(\lambda^3)$$

Second Order Wave Function

In general, the correction to the wave function is more significantly more involved than the energy. It is not always needed. The second order wave function correction is used for many applications:

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle + \lambda \sum_{k \neq n} \frac{\langle k^{(0)} | H | n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle \\ &+ \lambda^2 \sum_{\ell \neq n} \sum_{k \neq n} \frac{\langle k^{(0)} | H | \ell^{(0)} \rangle \langle \ell^{(0)} | H | n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)}) (E_n^{(0)} - E_\ell^{(0)})} |k^{(0)}\rangle \\ &+ \lambda^2 \sum_{k \neq n} \frac{\langle k^{(0)} | H | n^{(0)} \rangle^2}{(E_n^{(0)} - E_k^{(0)})^2} \left(|k^{(0)}\rangle - \frac{1}{2} |n^{(0)}\rangle \right) \end{aligned}$$

Relativistic correction

For heavy atoms electron motion is sufficiently rapid that one should consider the relativistic kinetic energy,

$$\hat{K} = \sqrt{(\hat{p}c)^2 + (mc^2)^2} - mc^2$$

We can rewrite the relativistic kinetic energy as,

$$\hat{K} = mc^2 \sqrt{1 + \left(\frac{\hat{p}c}{mc^2}\right)^2} - mc^2$$

and apply a Taylor's series

$$\sqrt{1 + x^2} = 1 + \frac{x^2}{2} - \frac{x^4}{8} + \dots$$

Kinetic energy operator

To obtain the zero order kinetic energy and series of relativistic corrections.

$$\hat{K} = \frac{\hat{p}^2}{2m} - \frac{\hat{p}^4}{8c^2m^3} + \frac{\hat{p}^6}{16c^4m^5}$$

The different orders are shown as follows

$$\hat{K}^{(0)} = \frac{\hat{p}^2}{2m} \quad \hat{K}^{(1)} = -\frac{\hat{p}^4}{8c^2m^3} \quad \hat{K}^{(2)} = \frac{\hat{p}^6}{16c^4m^5}$$

The relative magnitude of the first order correction to the zero order energy is

$$\frac{\hat{K}^{(1)}}{\hat{K}^{(0)}} = \frac{\hat{p}^2}{(2mc)^2}$$

This correction is of the order of 2×10^{-5} . For this reason we will consider the first order correction $K^{(1)}$, but not the second order correction, $K^{(2)}$.

According to first order perturbation theory the energy correction is

$$\langle n\ell m | \hat{K}^{(1)} | n\ell m \rangle = - \langle n\ell m | \frac{\hat{p}^4}{8c^2 m^3} | n\ell m \rangle$$

From the equation above we find that we can write the first order energy as

$$\hat{K}^{(1)} = - \frac{1}{2mc^2} (\hat{K}^{(0)})^2$$

This permits us to write the first order correction to the kinetic energy as the square of the zero order kinetic energy.

$$\langle n\ell m | \hat{K}^{(1)} | n\ell m \rangle = - \frac{1}{2mc^2} \langle n\ell m | (\hat{K}^{(0)})^2 | n\ell m \rangle$$

We can conveniently use the definition of the hamiltonian to write this further as

$$- \frac{1}{2mc^2} \langle n\ell m | \left(\hat{H}^{(0)} - \frac{e^2}{4\pi\epsilon_0 r} \right)^2 | n\ell m \rangle$$

Relativistic correction

There are three terms in the expansion of the operator:

$$\langle n\ell m | (\hat{H}^{(0)})^2 | n\ell m \rangle = (E^{(0)})^2$$

The cross term is:

$$2 \langle n\ell m | \hat{H}^{(0)} \frac{e^2}{4\pi\epsilon_0 r} | n\ell m \rangle = 2E^{(0)} \frac{e^2}{4\pi\epsilon_0} \langle n\ell m | \frac{1}{r} | n\ell m \rangle = -4(E^{(0)})^2$$

Here we have used the virial theorem, which tells us that

$$\frac{e^2}{4\pi\epsilon_0} \langle n\ell m | \frac{1}{r} | n\ell m \rangle = -2E^{(0)}$$

The final term is

$$\frac{e^4}{(4\pi\epsilon_0)^2} \langle n\ell m | \frac{1}{r^2} | n\ell m \rangle \rightarrow \frac{e^4}{(4\pi\epsilon_0)^2} \frac{1}{a_0^2 n^3 (\ell + 1/2)}$$

We do not show the integration here, but it can be found in many quantum mechanics textbooks.

Relativistic correction

Combining the three terms we find that

$$\langle n\ell m | \hat{K}^{(1)} | n\ell m \rangle = -\frac{(E^{(0)})^2}{2mc^2} \left(\frac{4n}{\ell + 1/2} - 3 \right)$$

Although the relativistic correction is small for hydrogen and other light elements, it becomes significant for heavier elements. We find that the relativistic hamiltonian should be used for second and third row transition elements, lanthanides and actinides.

Spin-orbit coupling

The spin-orbit operator is

$$\hat{H}_{SO}^{(1)} = -\mu_e \cdot \vec{B}_p$$

The spin magnetic moment arises in the frame of reference of the electron due to the relative motion of the proton. Thus, B_p arises as the result of a Biot-Savart current produced by the proton as the electron moves around it. The spin-orbit hamiltonian depends on both S and L.

$$\hat{H}_{SO}^{(1)} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \hat{S} \cdot \hat{L}$$

The total angular momentum is

$$\hat{J} = \hat{S} + \hat{L}$$

While neither L nor S commutes with $L \cdot S$

$$[\hat{L} \cdot \hat{S}, \hat{L}] = i\hbar(\hat{L} \times \hat{S})$$

$$[\hat{L} \cdot \hat{S}, \hat{S}] = i\hbar(\hat{S} \times \hat{L})$$

Spin-orbit coupling

The total angular momentum J commutes with $L \cdot S$

$$[\hat{L} \cdot \hat{S}, \hat{J}] = [\hat{L} \cdot \hat{S}, \hat{S}] - [\hat{L} \cdot \hat{S}, \hat{L}] = 0$$

The two commutators $[L \cdot S, S]$ and $[L \cdot S, L]$ cancel since in general

$$(\hat{A} \times \hat{B}) = -(\hat{B} \times \hat{A})$$

and therefore the same is true of $L \times S$ and $S \times L$.

Since neither S nor L commute with $L \cdot S$ then they change in time.

$$\hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L} \cdot \hat{S}$$

This expression is conveniently used to evaluate $\hat{L} \cdot \hat{S}$

$$\hat{L} \cdot \hat{S} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

Spin-orbit coupling

This is a very useful expression that permits evaluation of the coupling of two angular momenta. Thus, to evaluate $\hat{H}_{SO}^{(1)}$ we can use this expression combined with the expectation value of $1/r^3$.

$$\langle n\ell m \left| \frac{1}{r^3} \right| n\ell m \rangle = \frac{1}{a_0^2 n^3 \ell(\ell + 1)(\ell + 1/2)}$$

From the first order perturbation theory we have

$$E_{SO}^{(1)} = \langle n\ell m \left| \hat{H}_{SO}^{(1)} \right| n\ell m \rangle = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2} \langle n\ell m \left| \frac{\hat{S} \cdot \hat{L}}{r^3} \right| n\ell m \rangle$$

The final result is

$$E_{SO}^{(1)} = \frac{(E^{(0)})^2}{2mc^2} \left(\frac{n[j(j + 1) - \ell(\ell + 1) - 3/4]}{\ell(\ell + 1)(\ell + 1/2)} \right)$$

Spin-orbit coupling

We have used the fact that $s = 1/2$ so that $s(s+1) = 3/4$. There is a combined correction that involves both the relativistic and spin-orbit contributions. The combined result is known as the fine structure correction to the energy. The fine structure correction is

$$E_{fs}^{(1)} = \frac{(E^{(0)})^2}{2mc^2} \left(3 - \frac{4n}{j + 1/2} \right)$$

The Variation Method

The variational theorem

The He atom

The variational theorem

The variation method allows us to obtain an approximation to the ground state energy of the system without solving the Schrödinger equation.

The variation method is based on the following theorem:

Given a system with hamiltonian operator H , then if ϕ is any normalized well-behaved function that satisfies the boundary conditions it is true that

$$\int \phi^* H \phi d\tau \geq E_0$$

where E_0 is the true value of the lowest energy eigenvalue of H . This important theorem allows us to calculate an upper bound for the ground state energy.

Practical significance

The variation method serves as the basis for all methods that use combinations of hydrogen-like orbitals to solve for the eigenfunctions (wave functions) and eigenvalues (energies) of atoms and molecules.

The radial part of the hydrogen-like wave functions is modified by a variational parameter, which is minimized. The theorem allows us to set the derivative with respect to any parameter α equal to zero to find the value of that parameter that minimizes the energy:

$$\frac{\partial}{\partial \alpha} \int \phi^* H \phi d\tau = 0$$

We can be sure that the energy calculated in this way will be greater than the true energy (an upper bound).

The hamiltonian for H

The electronic hamiltonian for the hydrogen atom consists of a kinetic energy term for the electron and the Coulomb attraction of the electron and proton (nucleus).

$$-\frac{\hbar^2}{2m} \nabla^2$$
$$-\frac{Ze^2}{r_1}$$

Of course, the nuclear charge of hydrogen is $Z = 1$ so the Z is included for completeness. We know that the solutions of the Schrödinger equation ($H\Psi = E\Psi$) gives energy levels:
 n is the principal quantum number.
 a_0 is the Bohr radius.

$$E_n = -\frac{e^2}{2a_0} \frac{1}{n^2}$$

The hamiltonian for He

For helium the same kinetic energy and Coulomb attraction terms are present, but there is also a Coulomb repulsion between the two electrons that must be included.

The diagram illustrates the components of the Hamiltonian for a two-electron system (Helium). It features a central blue circle with two plus signs (++) representing the nucleus. Two pink circles with minus signs (-) represent the electrons. Arrows point from the nucleus to each electron, labeled with the attraction terms $-\frac{Ze^2}{r_1}$ and $-\frac{Ze^2}{r_2}$. An arrow points from one electron to the other, labeled with the repulsion term $\frac{e^2}{r_{12}}$. On the far left and right, the kinetic energy terms are shown as $-\frac{\hbar^2}{2m} \nabla_1^2$ and $-\frac{\hbar^2}{2m} \nabla_2^2$ respectively.

Because of the Coulomb repulsion there is no exact solution for He. To solve the problem we use two 1s orbitals from the solution for hydrogen and then apply the variational method.

The He wave function

The hydrogen 1s wave functions for electrons 1 and 2 are:

$$f_1 = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a}\right)^{3/2} e^{-Zr_1/a}, f_2 = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a}\right)^{3/2} e^{-Zr_2/a}$$

The aufbau approach for atoms assumes that the total wave function for a many-electron atom is just a product of one electron wave functions. In the present case:

$$\phi = f_1 f_2$$

Note that the hydrogen wave functions are normalized so:

$$\int f_1^* f_1 d\tau = \int f_2^* f_2 d\tau = 1$$

Variational approach for the He atom

The He wave function used for the variation method is a product of two hydrogen 1s orbitals. However, instead of the nuclear charge Z we use a variational parameter ζ .

$$\varphi = \frac{1}{\pi} \left(\frac{\zeta}{a_0} \right)^3 e^{-\zeta r_1/a_0} e^{-\zeta r_2/a_0}$$

ζ has a physical interpretation. Since one electron tends to screen the other from the nucleus, each electron is subject to a nuclear charge that is less than Z .

The hamiltonian is:

$$H = \left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\zeta e^2}{r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{\zeta e^2}{r_2} \right) + (\zeta - Z) \frac{e^2}{r_1} + (\zeta - Z) \frac{e^2}{r_2} + \frac{e^2}{r_{12}}$$

Evaluation of the integrals

If we consider only the part of the hamiltonian in parentheses
We have the solution to a hydrogen atom with two electrons
in the 1s orbital.

$$\left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\zeta e^2}{r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{\zeta e^2}{r_2} \right) \varphi = -\zeta^2 \frac{e^2}{a_0} \varphi$$

where the right hand side is twice the energy of a 1s electron.
Using this result we have:

$$\int \varphi^* H \varphi d\tau = -\zeta^2 \frac{e^2}{a_0} \int \varphi^* \varphi d\tau + (\zeta - Z)e^2 \int \frac{\varphi^* \varphi d\tau}{r_1} + (\zeta - Z)e^2 \int \frac{\varphi^* \varphi d\tau}{r_2} + e^2 \int \frac{\varphi^* \varphi d\tau}{r_{12}}$$

The integrals have the following values:

$$\int \varphi^* \varphi d\tau = 1 \quad , \quad \int \frac{\varphi^* \varphi d\tau}{r_1} = \int \frac{\varphi^* \varphi d\tau}{r_2} = \frac{\zeta}{a_0} \quad , \quad e^2 \int \frac{\varphi^* \varphi d\tau}{r_{12}} = \frac{5\zeta e^2}{8a_0}$$

Evaluation of the variational parameter ζ

We have:

$$\int \varphi^* H \varphi d\tau = \left(\zeta^2 - 2Z\zeta + \frac{5}{8}\zeta \right) \frac{e^2}{a_0}$$

We now vary ζ to minimize the variational integral:

$$\frac{\partial}{\partial \zeta} \int \varphi^* H \varphi d\tau = \frac{\partial}{\partial \zeta} \left(\zeta^2 - 2Z\zeta + \frac{5}{8}\zeta \right) \frac{e^2}{a_0} = 0$$

$$2\zeta - 2Z + \frac{5}{8} = 0$$

$$\zeta = Z - \frac{5}{16}$$

The variational energy is:

$$\int \varphi^* H \varphi d\tau = \left(-Z^2 + \frac{5}{8}Z - \frac{25}{256} \right) \frac{e^2}{a_0} = - \left(Z - \frac{5}{16} \right)^2 \frac{e^2}{a_0}$$

The variational energy: comparison with experiment

The experimental ionization energy of He is -24.5 eV.

Our first guess would be to calculate the energy of the 1s Electron in He using the hydrogen energy level with a nuclear charge $Z = 2$, $E = -Ze^2/a_0$.

This gives $-2(13.6)$ eV = -27.2 eV.

Using the value obtained by the variational method we have, $E = -(27/16)e^2/a_0 = -(27/16)(13.6)$ eV = -22.95 eV.

The value is much closer to the true value. In accord with the variational theorem, the true ground state energy is less than that given by variational method.

Summary for the variational principle

The hydrogen atom is the only atom with an exact solution.

Hydrogen wave functions are used as the approximation for atomic wave functions in multielectron atoms.

The variational principle states that any wave function we choose that satisfies the Schrödinger equation will give an energy greater than the true energy of the system.

The variation method provides a general prescription for improving on any wave function with a parameter by minimizing that function with respect to the parameter.