2H43 THEORETICAL CHEMISTRY

Calculation of Atomic (and Molecular) Properties

THE VARIATIONAL PRINCIPLE

Our aim is to solve the time-independent Schrödinger equation.

$$H\Psi = E\Psi \tag{4.1}$$

Only in a very few cases can we solve this equation exactly. We would like to be able to calculate approximate solutions to equation (4.1) and be able to have some feel for how reliable they are. We thus try to produce a wavefunction such that

$$\Phi \simeq \Psi \tag{4.2}$$

So, how do we determine Φ how accurate is it and how may we compare different approximate Φ?

To address this question we start rather more generally. We consider a general eigenvalue problem corresponding to equation (4.1).

$$\hat{A}f_n = a_n f_n \tag{4.3}$$

Here $\hat{A}$ is both Hermitian and linear, as our Hamiltonian would normally be. (Hermitian: $\langle f_1 | \hat{A} | f_2 \rangle = \langle f_2 | \hat{A} | f_1 \rangle^*$. Linear: $\hat{A}(c_1 f_1 + c_2 f_2) = c_1 \hat{A} f_1 + c_2 \hat{A} f_2$). Given that $\hat{A}$ is Hermitian all the eigenvalues a_n are real.

$$\hat{A}f_n = a_n f_n \qquad \hat{A}f_m = a_m f_m$$

$$\langle f_m | \hat{A} | f_n \rangle = \langle f_m | \hat{A} f_n \rangle = \langle f_m | a_n f_n \rangle = a_n \langle f_m | f_n \rangle$$

$$\langle f_m | \hat{A} | f_n \rangle = \langle f_n | \hat{A} | f_m \rangle^* = \langle f_n | \hat{A} f_m \rangle^* = \langle f_n | a_m f_m \rangle^* = a_m^* \langle f_n | f_m \rangle^* = a_m^* \langle f_m | f_n \rangle$$

Thus $(a_n - a_m^*)\langle f_m | f_n \rangle = 0$ and a_n is real for $n = m$.

We shall assume that there is a smallest eigenvalue and sort them into value order

$$a_0 \le a_1 \le a_2 \le \cdots \le a_{n-1} \le a_n \le a_{n+1} \le \cdots \tag{4.4}$$

We also need to assume (and are able to without losing generality) that the eigenvalues in equation (4.3) are orthonormal. In other words

$$\langle f_m | f_m \rangle = \delta_{n,m} \tag{4.5}$$

The expectation values of experimental observables for a given system in a given state are calculated as the matrix elements of (normalised) eigenfunctions. This is a fundamental principle of quantum theory. If we know our system is in state f_n then the expectation value for some operator $\hat{O}$ is given as

$$\frac{\langle f_n | \hat{O} | f_n \rangle}{\langle f_n | f_n \rangle} \tag{4.6}$$

A special case is the trivial case that $\hat{O} = \hat{A}$ and that $n = 0$. Then equation (4.6) takes the form

$$\frac{\langle f_n|\hat{O}|f_n\rangle}{\langle f_n|f_n\rangle} = \frac{\langle f_0|\hat{A}|f_0\rangle}{\langle f_0|f_0\rangle} = \frac{\langle f_0|a_0 f_0\rangle}{\langle f_0|f_0\rangle} = \frac{a_0\langle f_0|f_0\rangle}{\langle f_0|f_0\rangle} = a_0 \qquad (4.7)$$

We now ask ourselves what happens to the above expectation value when we replace f_0 with and approximate function

$$f_0 \simeq \phi \qquad (4.8)$$

The idea is that ϕ may be chosen freely. It may be chosen so that the integrals entering

$$\frac{\langle \phi|\hat{A}|\phi\rangle}{\langle \phi|\phi\rangle} \qquad (4.9)$$

can be evaluated. Further it is to be stressed that by evaluating (4.9) we need know nothing about the exact function. There now arises the question: if two different approximate functions have been suggested, how may we differentiate between them. Can one be judged better than the other? (What, in this case does "better" really mean?) To answer this question partly we use the completeness of the set of eigenfunctions and expand our test function of equation (4.8) as

$$\phi = \sum_n c_n f_n \qquad (4.10)$$

Fortunately we only need to know that this expansion is in principle possible, not its precise form. We then insert this into equation (4.9) and use the fact that the operator $\hat{A}$ is a linear operator.

$$\frac{\langle \phi|\hat{A}|\phi\rangle}{\langle \phi|\phi\rangle} = \frac{\left\langle \sum_n c_{n_1} f_{n_1}\left|\hat{A}\right|\sum_n c_{n_2} f_{n_2}\right\rangle}{\left\langle \sum_n c_{n_1} f_{n_1}\left|\sum_n c_{n_2} f_{n_2}\right.\right\rangle} = \frac{\left\langle \sum_n c_{n_1} f_{n_1}\left|\sum_n c_{n_2}\hat{A} f_{n_2}\right.\right\rangle}{\left\langle \sum_n c_{n_1} f_{n_1}\left|\sum_n c_{n_2} f_{n_2}\right.\right\rangle}$$

$$= \frac{\left\langle \sum_n c_{n_1} f_{n_1}\left|\sum_n c_{n_2} a_{n_2} f_{n_2}\right.\right\rangle}{\left\langle \sum_n c_{n_1} f_{n_1}\left|\sum_n c_{n_2} f_{n_2}\right.\right\rangle} = \frac{\sum_{n_1,n_2}\left\langle c_{n_1} f_{n_1}\left|c_{n_2} a_{n_2} f_{n_2}\right.\right\rangle}{\sum_{n_1,n_2}\left\langle c_{n_1} f_{n_1}\left|c_{n_2} f_{n_2}\right.\right\rangle}$$

$$= \frac{\sum_{n_1,n_2} c_{n_1}^* c_{n_2} a_{n_2}\left\langle f_{n_1}|f_{n_2}\right\rangle}{\sum_{n_1,n_2} c_{n_1}^* c_{n_2}\left\langle f_{n_1}|f_{n_2}\right\rangle} = \frac{\sum_{n_1,n_2} c_{n_1}^* c_{n_2} a_{n_2}\delta_{n_1,n_2}}{\sum_{n_1,n_2} c_{n_1}^* c_{n_2}\delta_{n_1,n_2}}$$

$$= \frac{\sum_n c_n^* c_n a_n}{\sum_n c_n^* c_n} = \frac{\sum_n |c_n|^2 a_n}{\sum_n |c_n|^2}$$

$$\geq \frac{\sum_n |c_n|^2 a_0}{\sum_n |c_n|^2} = \frac{a_0 \sum_n |c_n|^2}{\sum_n |c_n|^2} = a_0 \qquad (4.11)$$

Let us take a one-dimensional case with a single particle in a potential well.
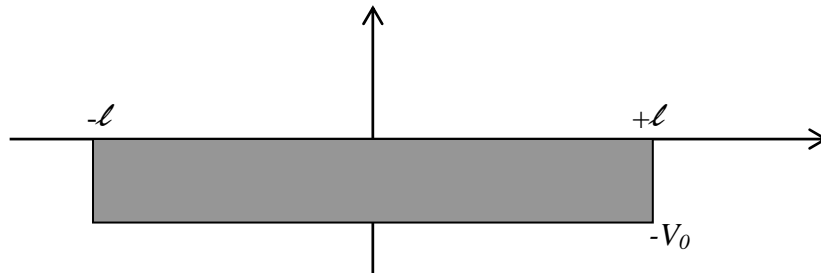
The profile of the well is shown above and is given by

$$V(x) = \begin{cases} -V_0 & \text{for } |x| \le l \\ 0 & \text{for } |x| > l \end{cases} \tag{4.12}$$

The Schrödinger equation for this particle is given by

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right]\Psi(x) = E\Psi(x) \tag{4.13}$$

The Hamiltonian is obviously

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{4.14}$$

The ground state is the state of the lowest energy. We propose the approximate function

$$\phi = \exp\left(-\alpha x^2\right). \tag{4.15}$$

The "best" α will most likely lie somewhere in between. It can, however, be determined by variation. Thus the quantity

$$\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \tag{4.16}$$

becomes a function of α.

$$\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \equiv \tilde{E}(\alpha) \tag{4.17}$$

This energy is always greater than (or at best equal to) the ground state energy. We then determine α by requiring

$$\frac{\partial}{\partial \alpha}\tilde{E}(\alpha) = 0 \tag{4.18}$$

The function given by our test function with the appropriate value of α inserted is then taken to be the "best" wavefunction for this particular family.

Variation (General)

In the general case

$$\hat{A}f_0 = a_0 f_0 \qquad (4.19)$$

The eigenfunction f_0 depends on the coordinates of the problem. In the case above on the *x*-coordinate. In any other case there will be more coordinates so that we might write our test function

$$\phi = \phi\left(p_1, p_2, \ldots, p_{N_p}; \vec{x}\right) \qquad (4.20)$$

As above we write

$$\frac{\langle\phi|\hat{A}|\phi\rangle}{\langle\phi|\phi\rangle} \equiv \tilde{a}\left(p_1, p_2, \ldots, p_{N_p}\right) \qquad (4.21)$$

As a result each of the new coordinates have to be determined

$$\frac{\partial a\left(p_1, p_2, \ldots, p_{N_p}\right)}{\partial p_1} = \frac{\partial a\left(p_1, p_2, \ldots, p_{N_p}\right)}{\partial p_2} = \cdots = \frac{\partial a\left(p_1, p_2, \ldots, p_{N_p}\right)}{\partial p_{N_p}} = 0 \qquad (4.22)$$

We may introduce more and more parameters in order to get a more and more exact solution. The problem arises because these equations rapidly become too unwieldy to be solvable.

The Hydrogen atom again

The Hamiltonian for the single electron of the hydrogen atom is (as we have seen before)

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \qquad (4.23)$$

where we have assumed that the nucleus is placed at the origin.

In order to avoid carrying the "baggage" of fundamental constants around we shall work here in atomic units. For this we set

$$\hbar = m = |e| = 4\pi\varepsilon_0 = 1 \qquad (4.24)$$

Lengths are then given in Bohr (=0.5292 Å) and energies in Hartrees (1 Hartree = 27.21 eV). With these the Hamiltonian becomes

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} \qquad (4.25)$$

The eigenvalue problem

$$\hat{H}\psi_n = e_n\psi_n \qquad (4.26)$$

has as its lowest eigenvalue

$$e_0 = -\frac{1}{2} \qquad (4.27)$$

and the corresponding eigenfunction is

$$\psi_0 = \frac{1}{\sqrt{\pi}} e^{-r} \tag{4.28}$$

(this function is normalized) as can be found in most introductory textbooks on quantum theory.

Since we in this case know the exact solution we can directly compare it with results of calculations using the variational method. This is in almost all other cases impossible.

We will apply the variational method for the test function

$$\phi = \left(\frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2} \tag{4.29}$$

i.e. a Gaussian (that furthermore is normalized). In the overhead we compare the exact wavefunction with that of (4.29) for different values of α.

Since ϕ of equation (4.29) is normalised the expectation value of equation (4.21) becomes

$$\tilde{E}(\alpha) = \frac{3\alpha}{2} - 2 \left(\frac{2\alpha}{\pi} \right)^{\frac{1}{2}} \tag{4.30}$$

Taking the derivative of this with respect to α gives the value of α at the minimum

$$\alpha = \frac{8}{9\pi} \simeq 0.283 \tag{4.31}$$

and the expectation value of this value of α is

$$\tilde{E}\left(\alpha = \frac{8}{9\pi} \right) = -\frac{4}{3\pi} \simeq -0.424 \tag{4.32}$$

By looking at our plots we can see that this is reasonable (but no more) description of the exact wavefunction although the agreement between the exact lowest energy and the approximate one may suggest a better agreement.

We may directly measure the quality of the approximate wavefunction in the present example by evaluating

$$O(\alpha) = \langle \phi - \psi | \phi - \psi \rangle \tag{4.33}$$

This function is a minimum when the difference between the exact and the approximate function is smallest. $O(\alpha)$ has a minimum at

$$\alpha \simeq 0.27 \tag{4.34}$$

i.e. for a value close to that of equation (4.31).