

## 8 The Variational Principle

### 8.1 Approximate solution of the Schroedinger equation

If we can't find an analytic solution to the Schroedinger equation, a trick known as the variational principle allows us to estimate the energy of the ground state of a system. We choose an unnormalized trial function  $\Phi(a_n)$  which depends on some *variational parameters*,  $a_n$  and minimise

$$E[a_n] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

with respect to those parameters. This gives an approximation to the wavefunction whose accuracy depends on the number of parameters and the clever choice of  $\Phi(a_n)$ . For more rigorous treatments, a set of basis functions with expansion coefficients  $a_n$  may be used.

The proof is as follows, if we expand the normalised wavefunction

$$|\phi(a_n)\rangle = \Phi(a_n) / \langle \Phi(a_n) | \Phi(a_n) \rangle^{1/2}$$

in terms of the true (unknown) eigenbasis  $|i\rangle$  of the Hamiltonian, then its energy is

$$E[a_n] = \sum_{ij} \langle \phi | i \rangle \langle i | \hat{H} | j \rangle \langle j | \phi \rangle = \sum_i |\langle \phi | i \rangle|^2 E_i = E_0 + \sum_i |\langle \phi | i \rangle|^2 (E_i - E_0) \geq E_0$$

where the true (unknown) ground state of the system is defined by  $\hat{H}|i_0\rangle = E_0|i_0\rangle$ . The inequality arises because both  $|\langle \phi | i \rangle|^2$  and  $(E_i - E_0)$  must be positive.

Thus the lower we can make the energy  $E[a_i]$ , the closer it will be to the actual ground state energy, and the closer  $|\phi\rangle$  will be to  $|i_0\rangle$ .

If the trial wavefunction consists of a complete basis set of orthonormal functions  $|\chi_i\rangle$ , each multiplied by  $a_i$ :  $|\phi\rangle = \sum_i a_i |\chi_i\rangle$  then the solution is exact and we just have the usual trick of expanding a wavefunction in a basis set. Alternately, we might just use an incomplete set with a few low-energy basis functions to get a  $|\Phi\rangle$  close to the ground state  $|i_0\rangle$ . In practice, this is how most quantum mechanics problems are solved.

### 8.2 Excited States

The variational method can be adapted to give bounds on the energies of excited states, under certain conditions. Suppose we choose a trial function  $\Phi_1(\beta_n)$  with variational parameters  $\beta_n$ , which is made orthogonal to the ground state  $\phi_0$ , by imposing the condition  $\langle \phi_0 | \phi_1 \rangle = 0$ .

If we know  $|\phi_0\rangle = |i_0\rangle$ , then similar to the above

$$E[a_n] = \frac{\langle \Phi_1 | \hat{H} | \Phi_1 \rangle}{\langle \Phi_1 | \Phi_1 \rangle} = \sum_{ij} \langle \phi_1 | i \rangle \langle i | \hat{H} | j \rangle \langle j | \phi_1 \rangle = \sum_i |\langle \phi_1 | i \rangle|^2 E_i = 0 + E_1 + \sum_{i=2} |\langle \phi_1 | i \rangle|^2 (E_i - E_1) \geq E_1$$

So the variational method gives an upper bound on the first excited-state energy, and so on. We can satisfy  $\langle i_0 | \phi_1 \rangle = 0$  if  $|i_0\rangle$  is known, *or* if it has a known symmetry from which we can exploit (e.g. if  $|i_0\rangle$  has even parity, choosing  $|\Phi_1\rangle$  to be odd.)

In general, though, we only have a variational estimate of the ground state  $\phi_0(\alpha_n)$ . In this case the expression above, subject to the constraint  $\langle \phi_1(\beta_n) | \phi_0(\alpha_n) \rangle = 0$ , gives an estimate of  $E_1$ . However, the error in this approach will be larger than for  $E_0$  because not only is the wavefunction incorrect, but also the constraint  $\langle \phi_1 | \phi_0 \rangle = 0$  is not quite correct; using an approximate ground state does not guarantee that we get an upper bound for the excited states.

If the excited state has different symmetry from those of the lower-lying levels, and we choose trial functions with the correct symmetries, orthogonality is guaranteed and we get an upper bound to the energy of the lowest-lying level with those symmetries, which is the excited state.

### 8.3 Analytic example of variational method - Binding of the deuteron

Say we want to solve the problem of a particle in a potential  $V(r) = -Ae^{-r/a}$ . This is a model for the binding energy of a deuteron due to the strong nuclear force, with  $A=32\text{MeV}$  and  $a=2.2\text{fm}$ . The strong nuclear force does not exactly have the form  $V(r) = -Ae^{-r/a}$ , unlike the Coulomb interaction we don't know what the exact form should be, but  $V(r) = -Ae^{-r/a}$  is a reasonable model.

The potential is spherically symmetric, most attractive at  $r = 0$  and falls rapidly to zero at large  $r$ , so we choose a trial wavefunction which does the same, say  $\phi = ce^{-\alpha r/2a}$ . This has only one dimensionless variational parameter,  $\alpha$ . The value of  $c$  follows from normalisation  $\int c^2 e^{-\alpha r/a} 4\pi r^2 dr = 1$ ; which gives  $c^2 = \alpha^3/8\pi a^3$ . (The  $4\pi r^2$  comes from the problem being three dimensional).

According to the variational principle, our best estimate for the ground state using this trial function comes from minimising  $\langle \phi | \hat{H} | \phi \rangle$  with respect to  $\alpha$ .

$$\begin{aligned} \langle \phi | H | \phi \rangle / \langle \phi | \phi \rangle &= \frac{-\hbar^2}{2m} \int_0^\infty c^2 \left( e^{-\alpha r/2a} \nabla^2 e^{-\alpha r/2a} \right) 4\pi r^2 dr - A \int_0^\infty c^2 \exp[-(\alpha + 1)r/a] 4\pi r^2 dr \\ &= \frac{\hbar^2 \alpha^2}{8ma^2} - A \left( \frac{\alpha}{\alpha + 1} \right)^3 \end{aligned}$$

From this we find the minimum for  $E(\alpha)$  at  $\alpha_0$

$$\frac{dE}{d\alpha} = \frac{\hbar^2 \alpha}{4ma^2} - 3A \left( \frac{\alpha^2}{(\alpha + 1)^4} \right) = 0 \quad \implies \quad \frac{(\alpha_0 + 1)^4}{\alpha_0} = 12Ama^2/\hbar^2$$

Solving for  $\alpha_0$  gives  $\alpha_0 = 1.34$ , and substituting back into  $\langle \phi | H | \phi \rangle$  gives  $E_0 = -2.14\text{MeV}$ .

This is fairly close to the exact solution for this potential, which can be obtained analytically as a Bessel function of  $\sqrt{8mA}(a/\hbar)e^{-r/2a}$  if you manage to spot that change of variables! The exact solution gives  $E_0 = -2.245\text{MeV}$ .

### 8.4 Quantum forces: the Hellmann-Feynman Theorem

For many systems one is often interested in *forces* as well as energies. If we can write the energy of a in state  $\phi$  as  $E = \langle \phi | \hat{H} | \phi \rangle$  and differentiate with respect to some quantity  $\alpha$  then

$$\frac{dE}{d\alpha} = \left\langle \frac{d\phi}{d\alpha} | \hat{H} | \phi \right\rangle + \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle + \langle \phi | \hat{H} | \frac{d\phi}{d\alpha} \rangle$$

But since  $\hat{H}|\phi\rangle = E|\phi\rangle$  and  $\langle \phi | \phi \rangle$  is 1 for normalisation:

$$\frac{dE}{d\alpha} = \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle + E \frac{d}{d\alpha} \langle \phi | \phi \rangle = \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle$$

This result is called the Hellmann-Feynman theorem: the first differential of the expectation value of the Hamiltonian with respect to *any quantity* does not involve differentials of the wavefunction.

e.g. if  $\alpha$  represents the position of a nucleus in a solid, then the force on that nucleus is the expectation value of the force operator  $\frac{d\hat{H}}{d\alpha}$ . It can be applied to any quantity which is a differential of the Hamiltonian provided the basis set does not change.

Caveat: if we use an incomplete basis set which depends explicitly the positions of the atoms, then we have  $|\phi\rangle = \sum_{n,i} |u_{n,i}(\mathbf{r})\rangle$ . This give spurious so-called ‘‘Pulay’’ forces if  $\phi$  is not an exact eigenstate.

## 8.5 An aside about Kinetic Energy

The expectation value of the kinetic energy  $\langle \hat{T} \rangle$  is always positive. This can be shown by an integration by parts in which the first term vanishes provided the wavefunction tends to zero at infinity (which it will for a bound state). In 1D:

$$\langle \hat{T} \rangle = \frac{-\hbar^2}{2m} \int \Phi^* \frac{d^2}{dx^2} \Phi dx = \frac{-\hbar^2}{2m} [\Phi^* \frac{d}{dx} \Phi]_{-\infty}^{\infty} + \frac{\hbar^2}{2m} \int \frac{d}{dx} \Phi^* \frac{d}{dx} \Phi dx = \frac{\hbar^2}{2m} \int \left| \frac{d}{dx} \Phi \right|^2 dx$$

The second term integrand is positive everywhere, so the kinetic energy is always positive.

## 8.6 Variational Method in MAPLE

The variational method is exceptionally well suited to computer algebra packages such as maple. The procedure is as follows:

- Define Trial wavefunction  $\Phi$
- Evaluate Normalization factor  $|c^2| = \langle \Phi | \Phi \rangle$
- Evaluate unnormalised kinetic energy  $\langle T \rangle = -\hbar^2 \langle \Phi | \nabla^2 | \Phi \rangle / 2m$
- Evaluate unnormalised potential energy  $\langle V \rangle = \langle \Phi | \hat{V} | \Phi \rangle$
- Differentiate with respect to variational parameters  $D_{a_n} = \frac{d}{da_n} (\langle T \rangle + \langle V \rangle) / c^2$
- Solve  $D_{a_n} = 0$  for all  $a_n$
- Substitute optimal value for  $a_n$  into  $\Phi$ .
- Evaluate  $[\langle T \rangle + \langle V \rangle] / c^2$  using optimised wavefunction.

If one needs to do another variational calculation for a different potential and trial wavefunction, only definitions 1 and 3 need to be changed.

## 8.7 Density functional theory (Nobel prize 1998)

If we consider the total probability density of a system of many interacting particles  $\rho(\mathbf{r})$ , there may be several possible wavefunctions which could give rise to it: call this set  $S(\Phi)$ .

Now, consider the expectation value of the energy  $\langle \hat{H} \rangle$ . We know from the variational principle that  $\langle \hat{H} \rangle \geq E_o$ . If we define a functional  $F[\rho(\mathbf{r})] = \text{Min}_{S(\Phi)} \langle \hat{H} \rangle$ , then it follows that  $F[\rho] \geq E_o$ .

Consequently we can use the variational principle to find the  $\rho(\mathbf{r})$  which minimises the value of F, and this may give us the ground state energy *without having to evaluate the wavefunction*. This is especially useful when the wavefunction consists of complex combinations of many different single-particle wavefunctions, as with the many electrons in a solid or molecule.

The drawback is that for interacting electrons, the functional is not known.

## 8.8 Kohn-Sham functional

For solids, we have  $10^{26}$  electron states. Analytic solution becomes impossible. In the past 20 years the density functional theory has come to dominate condensed matter physics, extending to chemistry, materials, minerals and beyond.

A popular form of DFT functional was introduced by Nobel laureate Walter Kohn and Lu Sham:

$$F(\rho) = T[\rho] + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}' + E_{xc}[\rho] + \sum_i \int \frac{Z_i e \rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{R}_i-\mathbf{r}'|} d^3\mathbf{r}'$$

Nobody has found a satisfactory functional for  $T$ . What is generally used is:

$$-\frac{\hbar^2}{2m} \sum_i \int \phi_i \nabla_i^2 \phi_i d^3\mathbf{r}$$

which is the kinetic energy of non-interacting ‘quasiparticles’ and depends explicitly on the wavefunctions. The integrals represent electrostatic interactions between the electrons and between electrons and ions, and  $E_{xc}$  is ‘everything else’. The advantage of this form is that it can be recast to give a set of one-particle equations with non-interacting fermions moving in an effective potential:

$$V_{eff} = \sum_{ion} \frac{Ze}{4\pi\epsilon_0|\mathbf{R}_{ion}-\mathbf{r}'|} + \int \frac{\rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

Since  $V_{eff}$  depends on  $\rho(\mathbf{r})$  these equations must be solved self-consistently.

Thus the density functional theorem shows that the problem of solving the Schroedinger equation for a collection of interacting electrons can be transformed to that of a system of non-interacting ‘quasiparticles’, with the cost that the Hamiltonian depends on the electron density  $\rho(\mathbf{r})$ :

$$H[\rho(\mathbf{r})]\phi_i = E_i\phi_i \quad \text{where} \quad \rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

Thus the Schroedinger equation is a nonlinear differential equation of many variables. Thus we must turn to the variational method. The most general approach here is to use a Fourier Series (plane wave basis set). The wavefunction for the  $i$ th electron is then written as

$$\phi_i = \sum_k c_{ik} \exp(-i\mathbf{k}\cdot\mathbf{r}) \quad \text{and the variational equation becomes:} \quad E_0 = \text{Min} \sum_i \langle \phi_i | \hat{H}(\rho) | \phi_i \rangle$$

The accuracy of the ground state energy of the electrons is determined by the number of Fourier components used. The wavefunctions are expanded in a computer-friendly basis set and the variational principle is used to transform the problem from a set coupled non-linear differential equations into a minimisation of a single function of many variables. Most structural properties of materials depend only on the electron ground state.

The single particle eigenstates of Kohn-Sham functional are not proper single electron states: indistinguishability means there is no such thing. Nevertheless, they are Bloch states, and they do exhibit well defined symmetry and energy ‘band-structure’ which can help with interpretation of the electronic structure