

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 β_n , which is made orthogonal to the ground state ϕ_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, α . 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 α .

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

From this we find the minimum for $E(\alpha)$ at α_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 α_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 ϕ as $E = \langle \phi | \hat{H} | \phi \rangle$ and differentiate with respect to some quantity α 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 α 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 ϕ 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 Φ
- 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 Φ .
- 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