5.5 The variational method

Most Hamiltonians can not be diagonalised exactly (i.e. their eigenvalue problem cannot be solved exactly). For these cases approximate methods have been developed.

Let's start with the ground state of the system.

Its energy satisfies

$$E_0 \leq E[\psi] \equiv \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \qquad \forall\ |\psi\rangle$$

If we knew the eigenstates of $\hat{H}$, we could expand

$$|\psi\rangle = \sum_E |E\rangle\langle E|\psi\rangle \qquad (\text{where } \hat{H}|E\rangle = E|\psi\rangle)$$

and write the above inequality as

$$E_0 = \frac{E_0 \sum_E |\langle E|\psi\rangle|^2}{\sum_E |\langle E|\psi\rangle|^2} \leq \frac{\sum_E E\,|\langle E|\psi\rangle|^2}{\sum_E |\langle E|\psi\rangle|^2} = \frac{\langle\psi|\left(\sum_E |E\rangle\langle E|\right)|\psi\rangle}{\langle\psi|\left(\sum_E |E\rangle\langle E|\right)|\psi\rangle}$$

$$\equiv E[\psi] \quad \forall\ |\psi\rangle$$

So, in principle, we could go through all states $|\psi\rangle \in \mathcal{H}$, work out the right hand side and find the $|\psi\rangle$ which gives the lowest expectation value for $\hat{H}$. This value would be the ground state energy, and the corresponding $|\psi_{min}\rangle = |\psi_0\rangle$ the ground state eigenvector.

Unfortunately, this is not practical, due to the infinite number of states $|\psi\rangle$ to go through. To restrict the number of states to go through, one selects a suitably

parametrized subset $|\psi(\alpha,\beta,\gamma,\dots)\rangle$ of states that have the general features expected of the true ground state, and then minimizes analytically the corresponding energy expectation value $E(\alpha,\beta,\gamma,\dots)$ with respect to the parameters $\alpha,\beta,\gamma,\dots$ The minimum value $E_{min} = E(\alpha_0,\beta_0,\gamma_0,\dots)$ is then an approximation to the ground state energy and provides an upper bound for E_0. The state $|\psi(\alpha_0,\beta_0,\gamma_0,\dots)\rangle$ is in general not an eigenstate of $\hat{H}$ and also not a particularly good approximation to the ground state. The quality of the upper bound $E_{min} = E(\alpha_0,\beta_0,\gamma_0,\dots) \geq E_0$ depends very much on how closely the parametrized states $|\psi(\alpha,\beta,\gamma,\dots)\rangle$ are able to capture the true shape of the ground state $|\psi_0\rangle$ for a suitable choice of parameters $\alpha_0,\beta_0,\gamma_0$.

- What is a suitable parametrization of $|\psi(\alpha,\beta,\gamma,\dots)\rangle$?

Consider a Hamiltonian of the general form

$$\hat{H} = \frac{\hat{\vec{p}}^{\,2}}{2M} + V(\hat{\vec{x}})$$

$$\text{Then } \langle\hat{H}\rangle_\psi = \frac{\frac{1}{2M}\langle\psi|\hat{\vec{p}}^{\,2}|\psi\rangle + \langle\psi|\hat{V}|\psi\rangle}{\langle\psi|\psi\rangle}$$

$$\left(\hat{\vec{p}}^{\,+} = \hat{\vec{p}}\right) = \frac{1}{2M}\frac{\langle\psi|\hat{\vec{p}}^{\,+}\cdot\hat{\vec{p}}|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|\hat{V}|\psi\rangle}{\langle\psi|\psi\rangle}$$

$$= \langle\hat{T}\rangle_\psi + \langle\hat{V}\rangle_\psi$$

In position space representation ($\psi(\vec{x}) = \langle \vec{x} | \psi \rangle$)

$$\langle \hat{T} \rangle_\psi = \frac{\hbar^2}{2M} \frac{\int d^3x \, |\vec{\nabla}\psi(\vec{x})|^2}{\int d^3x \, |\psi(\vec{x})|^2}$$

$$\langle \hat{V} \rangle_\psi = \frac{\int d^3x \, V(\vec{x}) |\psi(\vec{x})|^2}{\int d^3x \, |\psi(\vec{x})|^2}$$

To minimize $\langle \hat{T} \rangle$, $\psi(\vec{x})$ should be as flat as possible (no gradients). If the potential is attractive, its expectation value would be minimized by a $\psi(\vec{x})$ that is as tightly localized as possible at the position of the potential minimum. The wave function that minimizes $\langle \hat{H} \rangle_\psi$ thus must be a compromise — somewhat concentrated near the potential minimum, but with some spread and no unnecessary bumps and valleys — no nodes.

For $\hat{V}(\hat{\vec{x}}) = -\frac{e^2}{\hat{R}}$ (Coulomb), at the minimum of $\langle \hat{H} \rangle_\psi$ the kinetic and potential energies are related by the virial theorem: If we normalize our trial wave function $\psi(\vec{x})$ such that $\int d^3x \, |\psi(\vec{x})|^2 = 1$, the $\psi(\vec{x})$ has dimension $(\text{length})^{-3/2}$, so it must be of the form

$$\psi(\vec{x}) = \frac{1}{a^{3/2}} \psi\left(\frac{\vec{x}}{a}\right)$$ where $f(\vec{\xi})$ is a dimensionless function of the dimensionless argument $\vec{\xi} = \frac{\vec{x}}{a}$, and a is a length parameter that can be varied freely when we vary the wavefunction.

So, by changing the integration variable $\vec{x} \longrightarrow \vec{\xi}$,

$$\frac{\hbar^2}{2M}\int d^3x \left|\vec{\nabla}\psi(\vec{x})\right|^2 = \frac{\hbar^2}{2M}\, a^3 \int d^3\left(\frac{x}{a}\right)\left|\vec{\nabla}_x\left(\frac{1}{a^{3/2}} f\left(\frac{\vec{x}}{a}\right)\right)\right|^2$$

$$= \frac{\hbar^2}{2Ma^2}\int d^3\xi \left|\vec{\nabla}_\xi f(\xi)\right|^2$$

and

$$\int d^3x\, V(\vec{x})\left|\psi(\vec{x})\right|^2 = -e^2 \int a^3 d^3\xi\, \frac{1}{a\xi}\left|\frac{1}{a^{3/2}} f(\vec{\xi})\right|^2$$

$$= -\frac{e^2}{a}\int d^3\xi \frac{|f(\xi)|^2}{\xi}$$

So

$$E[a] = \langle \hat{H}\rangle_\psi[a] = \langle \hat{T}\rangle_\psi[a] + \langle \hat{V}\rangle_\psi[a] = \frac{1}{a^2}\underbrace{\langle \hat{T}\rangle_\psi[1]}_{t} + \frac{1}{a}\underbrace{\langle \hat{V}\rangle_\psi[1]}_{v}$$

Minimizing

$$0 = \frac{d}{da}E[a] = \frac{d}{da}\left(\frac{t}{a^2} + \frac{v}{a}\right) = -\frac{2t}{a^3} - \frac{v}{a^2} = \frac{1}{a}\left(-2\langle\hat{T}\rangle - \langle\hat{V}\rangle\right)$$

$$\Leftrightarrow \boxed{2\langle\hat{T}\rangle_\psi + \langle\hat{V}\rangle_\psi = 0 \quad \text{at the minimum}}$$

Virial theorem.

$$\Leftrightarrow \langle\hat{T}\rangle_\psi = -\frac{1}{2}\langle\hat{V}\rangle_\psi \quad \text{and} \quad \underbrace{\langle\hat{H}\rangle_\psi = \langle\hat{T}\rangle_\psi - 2\langle\hat{T}\rangle_\psi}_{= -\langle\hat{T}\rangle_\psi}$$

Example:

Consider $\hat{H} = \frac{\hat{p}^2}{2m} + \underbrace{\lambda \hat{x}^4}_{\hat{V}(\hat{x})}$ in 1 dimension

What are the expected features of the ground state?

1) The potential is even, so the ground state will have definite parity: $|\psi(x)|$ is even.

2) The ground state wavefunction will have no nodes (as argued above)

3) The expectation value $\langle \hat{x} \rangle_0 = 0$ in the ground state (since $|\psi(\vec{x})|^2$ is even), and $|\psi(x)|^2$ will be peaked around $x = 0$ to minimize $\hat{V}(\hat{x})$.

4) For normalizability, the ground state wave function will vanish at $x \to \infty$. This is also required to keep the potential energy finite.

5) Since $\hat{H}$ is positive definite, $E_0 \geq 0$.

A trial wave function that has these features and is also easy to work with (i.e. differentiate, integrate, ...) is

$$\psi(x, \alpha) = e^{-\alpha x^2/2} \qquad (\alpha > 0, \ \alpha \in \mathbb{R})$$

$$\Rightarrow E(\alpha) = \frac{\int_{-\infty}^{\infty} e^{-\alpha x^2/2} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \lambda x^4 \right) e^{-\alpha x^2/2}}{\int_{-\infty}^{\infty} dx \, e^{-\alpha x^2}}$$

$$= \frac{\int_{-\infty}^{\infty} \frac{d\xi}{\sqrt{\alpha}} e^{-\xi^2/2} \left(-\frac{\alpha \hbar^2}{2m} \frac{d^2}{d\xi^2} + \frac{\lambda}{\alpha^2} \xi^4 \right) e^{-\xi^2/2}}{\int_{-\infty}^{\infty} \frac{d\xi}{\sqrt{\alpha}} e^{-\xi^2}} \qquad (\alpha x^2 \equiv \xi^2$$

$$\Rightarrow E(\alpha) = \alpha \frac{\hbar^2}{4m} + \frac{3\lambda}{4\alpha^2}$$

To minimize $\langle \hat{T} \rangle$, α should be small, to minimize $\langle \hat{V} \rangle$, α should be large. ✓

Minimizing the energy, $\frac{dE}{d\alpha} = 0 = \frac{\hbar^2}{4m} - \frac{3\lambda}{2\alpha^3}$,

we find

$$\boxed{\alpha_0 = \left(\frac{6m\lambda}{\hbar^2}\right)^{1/3}}$$ for the optimal width parameter.

The corresponding minimal energy is

$$E(\alpha_0) = \frac{\hbar^2}{4m}\left(\frac{6m\lambda}{\hbar^2}\right)^{1/3} + \frac{3\lambda}{4}\left(\frac{\hbar^2}{6m\lambda}\right)^{2/3}$$

$$= \left(\frac{6\hbar^4\lambda}{64m}\right)^{1/3} + \left(\frac{27\hbar^4\lambda}{64 \cdot 36 m^2}\right)^{1/3} = \left(\frac{6\hbar^4\lambda}{m^2}\right)^{1/3}\left(\underbrace{\frac{1}{64^{1/3}}}_{1/4} + \underbrace{\frac{1}{(8\cdot 64)^{1/3}}}_{1/8}\right)$$

$$= \frac{3}{8}\left(\frac{6\hbar^4\lambda}{m^2}\right)^{1/3}$$

$$\Rightarrow \boxed{0 \leq E_0 \leq \frac{3}{8}\left(\frac{6\hbar^4\lambda}{m^2}\right)^{1/3}}$$

The best Gaussian approximation to the ground state wave function is

$$\boxed{\psi(x, \alpha_0) = \frac{\alpha_0}{\sqrt{2\pi}} e^{-\alpha_0 x^2/2} \quad \text{with } \alpha_0 = \left(\frac{6m\lambda}{\hbar^2}\right)^{1/3}}$$

How good is our bound? The calculation does not tell us the answer. We can try to add more parameters or tweak the functional form of our 1-parameter wavefunction. For example, since $V(x) = \lambda x^4$ grows faster at large x than the harmonic oscillator potential, the ground state wave function should decrease faster than a Gaussian (which is the harmonic oscillator ground state wave function). So we could try $\psi(x, \alpha, \beta) = e^{-\alpha x^2 - \beta x^4}$ to see how much lower we can push $E(\alpha, \beta)$. But for this ψ, we already have to do some integrals numerically.

We can keep adding parameters until our bound stops improving appreciably. At that point we give up, suspecting that the true E_0 value can not be much below our $E_{min}(\alpha_0, \beta_0, \ldots)$.

Note: if you choose $\psi(x, \alpha) = e^{-\frac{1}{2}\alpha x^2}$ as trial wavefunction for the harmonic oscillator ground state, the variational method gives the exact answer for the correct ground state energy $\frac{\hbar\omega}{2}$. But you don't know it! However, all your attempts to improve the wavefunction and lower the bound will fail — how frustrating!

Q: How well does the variational method work in cases where we know the answer?

Consider 2 examples:

Example 1:

Hydrogen atom with a Gaussian trial wave function for the ground state.

First: what do we expect?

True ground state wave function: $\psi_0(r) = \mathcal{N} e^{-r/a_0}$ (no angular dependence)

Trial wave function: $\psi(r,\alpha) = e^{-\alpha r^2}$; this falls off too steeply at $r \to \infty$ but has otherwise the correct symmetries and other general features

So let's see:

$$E(\alpha) = \frac{\int_0^\infty r^2 dr\, e^{-\alpha r^2} \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr} r^2 \frac{d}{dr} - \frac{e^2}{r}\right) e^{-\alpha r^2}}{\int_0^\infty r^2 dr\, e^{-2\alpha r^2}}$$

$$= \ldots = \frac{3\alpha\hbar^2}{2m} - e^2\sqrt{\frac{8\alpha}{\pi}}$$

(do this exercise, it might appear on an exam!)

This is minimal at $\alpha_0 = \left(\frac{me^2}{\hbar^2}\right)^2 \frac{8}{9\pi} = \frac{8}{9\pi}\frac{1}{a_0^2}$

with value

$$\boxed{E(\alpha_0) = -\frac{me^4}{2\hbar^2}\cdot\frac{8}{3\pi} = -0.85\, R_y}$$

This larger than the exact E_0, by about 15%. —

In this case the optimized trial wavefct. actually gives a surprisingly good estimate of the position uncertainty of the electron in the ground state:

$\Delta X(\alpha_0) = \sqrt{\frac{9\pi}{32}}\, a_0 \simeq 0.94 a_0$ (exact value: $(\Delta X)_0 = a_0$).

Usually the variational principle gives better accuracy for the energy than for the wavefunction.

Example 2

Ground state of helium: $\hat{H} \longrightarrow -\frac{\hbar^2}{2m}(\Delta_1 + \Delta_2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$

If we ignore the e-e interaction, the g.s. wave fct. is simply (up to a spin-singlet wave fct. for the spin that we ignore)

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)$$

(Of course, this ignores relativistic effects such as spin-orbit and spin-spin interactions.)

Here $\psi_{100}(\vec{r}) = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-Zr/a_0}$ $\quad (Z=2)$ $\quad (*)$

(independent of angles)

The corresponding energy (ignoring e-e int.) is

$$E = 2\left(-\frac{m(2e^2)^2}{2\hbar^2}\right) = -8\,Ry \simeq -108.8\,eV$$

The experimental value is $-78.6\,eV$. So simply ignoring the e-e interaction is a bad approximation, with almost 40% error.

But we can use the incorrect wave function (*) as a trial wave function, with the "effective nuclear charge" Z as a parameter. This effectively implements the idea that the main effect of the e-e interaction is to partially screen the central charge. With some algebra (see homework) one finds

$$E(Z) = \frac{\int d^3r_1\, d^3r_2\, \psi(r_1, r_2; Z)\left(-\frac{\hbar^2}{2m}(\Delta_1+\Delta_2) - 2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e}{|\vec{r}_1-\vec{r}_2|}\right)\psi(r_1, r_2; Z)}{\int d^3r_1\, d^3r_2\, |\psi(r_1, r_2; Z)|^2}$$

↑ depends on angles!

$$= \dots = -2R_y\left[\underbrace{4Z}_{V_1+V_2} \underbrace{-Z^2}_{T_1+T_2} \underbrace{-\frac{5}{8}Z}_{V_{ee}}\right]$$

This is minimized by

$$Z_{eff} = \frac{27}{16} = 2 - \frac{5}{16} \qquad \text{(screening!)}$$

with corresponding energy

$$E\left(2-\tfrac{5}{16}\right) = -2Z_{eff}^2 R_y \approx -77.5\,eV \quad > \quad E_0 = -78.6\,eV$$

This result is pretty accurate when compared with expt.!

Here we left the shape of the wave function unchanged, only rescaled its characteristic length, when turning on the e-e interaction. There is a priori no guarantee that this will faithfully capture what happens to the exact wavefunction when turning on that interaction. Why did this work so well?

In fact, there is a general principle behind this that shows that the variational energies will always be more accurate than the wavefunction: If the trial wavefunction and true wavefunction differ by $|\delta\psi\rangle$ then the energies differ at most by $O(\langle\delta\psi|\delta\psi\rangle) \sim O(\delta\psi^2)$. Let's see how this works:

Let $|E_0\rangle$ = true ground state (unknown, assumed to be normalized)

and $|\psi\rangle = |E_0\rangle + |\delta\psi\rangle$ the trial state.

Decompose $|\delta\psi\rangle$ into components parallel and perpendicular to $|E_0\rangle$:

$$|\delta\psi\rangle = |\delta\psi_\parallel\rangle + |\delta\psi_\perp\rangle \equiv \alpha|E_0\rangle + |\delta\psi_\perp\rangle$$

$$(\alpha = \langle E_0|\delta\psi\rangle)$$

The energy in the trial state is then

$$E[\psi] = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\left((1+\alpha^*)\langle E_0| + \langle\delta\psi_\perp|\right)\hat{H}\left((1+\alpha)|E_0\rangle + |\delta\psi_\perp\rangle\right)}{|1+\alpha|^2 + \langle\delta\psi_\perp|\delta\psi_\perp\rangle}$$

$$= \frac{E_0|1+\alpha|^2 + \langle\delta\psi_\perp|\hat{H}|\delta\psi_\perp\rangle}{|1+\alpha|^2 + \langle\delta\psi_\perp|\delta\psi_\perp\rangle} =$$

$$= \frac{E_0 + \langle\delta\psi_\perp|\hat{H}|\delta\psi_\perp\rangle/|1+\alpha|^2}{1 + \langle\delta\psi_\perp|\delta\psi_\perp\rangle/|1+\alpha|^2} = E_0\left(1 + O(\delta\psi_\perp)^2\right)$$

So the error in the energy is of <u>second order</u> in the error of the state vector. $|\delta\psi_\parallel\rangle$ actually produces no error at all in the energy. This is related to what we saw in perturbation theory where knowledge of the energy to $O(\hat{H}_{int}^n)$ required knowledge of the state only to $O(\hat{H}_{int}^{n-1})$.

Something similar holds for excited states:
Assume $|\psi_n\rangle = |E_n\rangle + |\delta\psi_n\rangle$ is a variational trial state for the n'th eigenstate $|E_n\rangle$.

Following the same steps:

$$|\delta\psi_n\rangle = \alpha_n |E_n\rangle + |\delta\psi_{n\perp}\rangle$$

$$E[\psi_n] = \frac{\langle\psi_n|\hat{H}|\psi_n\rangle}{\langle\psi_n|\psi_n\rangle} = \dots = \frac{E_n + \langle\delta\psi_{n\perp}|\hat{H}|\delta\psi_{n\perp}\rangle / |1+\alpha_n|^2}{1 + \langle\delta\psi_{n\perp}|\delta\psi_{n\perp}\rangle / |1+\alpha_n|^2}$$

$$= E_n \left(1 + O\left(\delta\psi_{n\perp}\right)^2\right)$$

Only in this case we cannot show that the correction is always positive. But what this shows is that

<u>the eigenkets of $\hat{H}$ are stationary points of $E[\psi]$</u>.

The ground state is a minimum of $E[\psi]$, namely the lowest stationary point of $E[\psi]$.