Lecture Notes of Quantum Mechanics

Translated by Yu Zhu

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Contents

List of Figures

Chapter 8

App. methods: variational approach

Fewest problems are exactly solved and we have to resort to approximate solution methods. The following approaches are available:

1. Approximate the problem with an exactly solvable problem; this approach is particularly suitable for understanding the structure of the solution.
2. Numerical solution via computer this strategy provides precise numbers, but often does not help understanding, and should therefore only be used last.
3. Variation Approach: Searching under a family of solutions that best understanding understanding of the solution structure and a good nose (for the approach) ahead, very elegant.
4. Perturbation calculation: Systematic improvement of the solution, good for developing the solution structure, can often provide exact figures.
5. Quasi-classic approximation: very physical, elegant, back-often-envelope arguments that reflect the relevant physics transparently

Point 1 was worked out in the previous chapters with some examples. Point 2 is dealt with in other lectures. We start with point 3, the variation approach. We will discuss the disturbance calculation in Chapter 9, and we will work on the quasi-classical approximation in Chapter 10.

The variation calculation is based on the Rayleigh-Ritz (RR) variation principle: Let Ψ be a state function, H a Hamiltonian with ground state energy E_0, then

$$\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0 \tag{8.1}$$

because with the own base φ_n to H

$$\begin{aligned}\langle\Psi|H|\Psi\rangle &= \sum_n \langle\Psi|\varphi_n\rangle \underbrace{\langle\varphi_n|H|\varphi_n\rangle}_{E_n\geq E_0} \langle\langle p_n|\Psi\rangle \\ &\geq E_0 \sum_n |\langle\Psi|\varphi_n\rangle|^2 \\ &= E_0\langle\Psi|\Psi\rangle\end{aligned} \tag{8.2}$$

This equation allows us to get an upper bound on the ground state energy (and the ground wave function Ψ_0): Take any Ψ, then $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$ gives an upper bound on E_0. We can write Ψ as

$$\Psi = \alpha\Psi_0 + \beta\Psi_0^\perp \tag{8.3}$$

where $\Psi_0^\perp \perp \Psi_0$. It is $\langle\Psi|\Psi\rangle = |\alpha|^2 + |\beta|^2$, so our Ψ the better the smaller the correction $\Psi_0^\perp$: the correct direction is to be found in Hilbert space H.

The RR principle also allows excited states to be estimated: If Ψ_0 is known, then the best function $\Psi - \langle\Psi_0|\Psi\rangle\Psi_0$ (with the lowest energy) gives the first excited state. The principle can be iterated for undegenerate problems: The optimization in

$$\mathcal{H}_\perp^N = \left\{ \Psi - \sum_{n=0}^{N-1} \langle\Psi_n|\Psi\rangle\, \Psi_n | \Psi_n = \text{EV to the } N-1 \text{ deepest EW } E_n \right\}$$

gives E_N and Ψ_N. In particular, one finds EN from the diagonalization of the matrix $\langle\Psi_k|H|\Psi_m\rangle$, with $\{\Psi_k\}$ a basis in $\mathcal{H}_N$; E_N is then the smallest representative of the largest eigenvalue λ in $\mathcal{H}_N$ with variation of $\mathcal{H}_N$. Or simply expressed in a formula, $E_N = \inf_{\mathcal{H}_N}\{\max_\lambda[EW(\langle\Psi_k|H|\Psi_m\rangle|\Psi_k, \Psi_m \in \mathcal{H}_N, \dim\mathcal{H}_N = N)]\}$. Symmetries can also be exploited: Let $SO(3)$ be a symmetry of H. Applying the RR principle in the subspaces $\mathcal{H}_l$ to the angular momentum $L^2 = \hbar^2 l(l+1)$ results in a barrier for the smallest energy with angular momentum $\hbar^2 l(l+1)$.

We can also get *lower* bounds, but this is generally much more difficult. A luck case is when $H = H_0 + V$ can be dismantled with $V \geq 0$. Let G be the ground state of H, then

$$\begin{aligned}E_G &= \langle\Psi_G|H|\Psi_G\rangle \\ &= \underbrace{\langle\Psi_G\,|H_0|\,\Psi_G\rangle}_{\geq E_0} + \underbrace{\langle\Psi|V|\Psi_G\rangle}_{\geq 0} \geq E_0\end{aligned} \tag{8.4}$$

In (8.4) we used that the ground state for H_0 with energy E_0 is generally given by $\Psi_0 \neq \Psi_G$, and thus $\langle \Psi_G | H_0 | \Psi_G \rangle \geq \langle \Psi_0 | H_0 | \Psi_0 \rangle = E_0$. In the following we look at an example.

8.1 Basic state of the He-atom

The helium atom consists of a nucleus with two electrons,

$$\mathrm{He} = \underbrace{2\mathrm{p} + 2\mathrm{n}}_{+2e \text{ charge}} + 2e^- \tag{8.5}$$

We only consider the electronic degrees of freedom and describe the two-particle problem of the electrons in the field of the nucleus. The Hamilton operator in the location display is

$$H = -\frac{\hbar^2}{2m}\left(\vec{\nabla}_1^2 + \vec{\nabla}_2^2\right) - 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \tag{8.6}$$

We know the ground state for an H-atom ($a_B = \hbar^2/m_e e^2$ the Bohr radius)

$$\Psi_0 = \left(\frac{1}{\pi a_B^3}\right)^{1/2} \exp\left(-\frac{r}{a_B}\right) \tag{8.7}$$

and use it to construct the variation approach

$$\Psi\left(\vec{r}_1, \vec{r}_2\right) = \frac{\alpha^3}{\pi a_B^3} \exp\left[-\alpha\left(r_1 + r_2\right)/a_B\right] \tag{8.8}$$

We will see later that this approach is compatible with the Pauli principle: the exact ground state of the He atom has the structure

$$\Psi\left(\vec{r}_1, s_1; \vec{r}_2, s_2\right) = \Psi_{\mathrm{Sym}}^{\mathrm{Bahn}}\left(\vec{r}_1, \vec{r}_2\right) \otimes \Psi_{\mathrm{Antisym}}^{\mathrm{Spin}}\left(s_1, s_2\right) \tag{8.9}$$

where s_i are the spin quantum numbers and sym / antisym indicates the symmetry of the function Ψ while swapping the variables. (8.8) has the right symmetry.

We have to calculate the expected value $\langle \Psi | H | \Psi \rangle$. For H-atoms, $E_0^{kin} = e^2/2a_B$ and $E^{pot} = -e^2/a_B$; because of the changed length $r \to \alpha r$ in (8.8) these energies are scaled according to

$$E^{\mathrm{kin}} = 2 \cdot \frac{e^2\alpha^2}{2a_B}, \quad E^{\mathrm{pot}} = -2 \cdot \frac{2e^2\alpha}{a_B} \tag{8.10}$$

where the doubling takes into account the presence of two electrons (the additional factor two in E^{pot} takes into account the doubled charge in the He nucleus). The calculation of the interaction energy

$$E^{\mathrm{WW}} = \left(\frac{\alpha^3}{\pi a_B^3}\right)^2 e^2 \iint \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 \frac{\exp\left[-2\alpha\left(r_1+r_2\right)/a_B\right]}{|\vec{r}_1 - \vec{r}_2|} \tag{8.11}$$

involves the following transformations: we use that $1/r$ is the Green's function of the Laplace operator,

$$\Delta(1/r) = -4\pi\delta^3(\vec{r}), \quad \mathcal{F}[1/r] = 4\pi/k^2 \tag{8.12}$$

and represent the coulom energy in the$\vec{k}$-space by the integral

$$\frac{e^2}{|\vec{r}_1 - \vec{r}_2|} = 4\pi e^2 \int \frac{d^3k}{(2\pi)^3} \frac{1}{k^2} \mathrm{e}^{i\vec{k}\cdot(\vec{r}_1 - \vec{r}_2)}$$

The integration over the location coordinate $\vec{r} = \vec{r}_1$ results (likewise with $\vec{r}_2$)

$$\begin{aligned} \int d^3 r \mathrm{e}^{i\vec{k}\cdot\vec{r} - 2\alpha r/a_B} &= \frac{4\pi}{k} \int_0^\infty dr\, \mathrm{Im}\left[r \mathrm{e}^{ikr - 2\alpha r/a_B}\right] \\ &= \frac{16\pi\alpha/a_B}{\left(k^2 + 4\alpha^2/a_B^2\right)^2} \end{aligned} \tag{8.13}$$

The remaining integration over $\vec{k}$ gives us the interaction energy

$$E^{\mathrm{WW}} = \frac{5\alpha}{8} \frac{e^2}{a_B} \tag{8.14}$$

This gives the total energy to

$$\langle H \rangle(\alpha) = \alpha^2 \frac{e^2}{a_B} - 4\alpha \frac{e^2}{a_B} + \frac{5}{8}\alpha \frac{e^2}{a_B} \tag{8.15}$$

it is minimized by $\alpha = 27/16$ and gives the following estimate for the ground state energy,

$$E_0 \leq -\left(\frac{27}{16}\right)^2 \frac{e^2}{a_B} \approx -2.85 e^2/a_B \tag{8.16}$$

This result is very close to the measured value $E_0 \approx -2.904 e^2/a_B$. Interpretation: Trivially we could expect $= 2$ since the charge is $Z = 2$. However, we find the reduced value $\alpha = 27/16 \leq 2$: each e^- shields the core for the other e^- with an effective charge $5/16$, as shown in sketch 8.1.

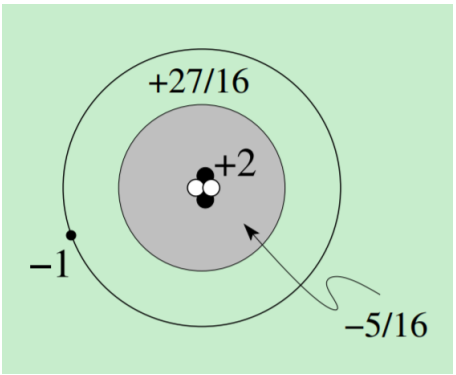

Figure 8.1: Shielding: the second electron (charge -1) moves in the middle field of the core (charge +2) and the first electron (effective shield charge -5/16); on the second electron thus acts an effective charge 27/16.