



Quantum Mechanics 2

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5 Chapter 8: The Variational Principle

Learning Goals

- To formulate the variational principle and apply it to different quantum systems to provide **upper bounds for their ground state energies**.
- To demonstrate that a **careful choice of test function** can lead to variational principle results that coincide with the exact solution of the Hamiltonian.
- To deploy the variational principle to construct a better approximation of the **ground state of the Helium** atom.
- To calculate from first principles the **effective electric charge** Z_{eff} of the helium atom, which previously was taken to be a phenomenological parameter extracted from data.

In this section of the lecture notes we present the main concepts discussed in **Chapter 8** (“**The Variational Principle**”) of the course textbook. The goal of these lecture notes is to provide a self-consistent study resource for the students, which is then complemented by the live lectures (and their recordings), the tutorial sessions, as well as their own study of the textbook. The relevant textbook sections are indicated below, material from other sections not listed there will not be required for the examination.

Textbook sections

- **8.1:** Theory
- **8.2:** The ground state of Helium

As we have seen through this course, unfortunately the number of quantum systems whose Hamiltonian admits an exact, analytic diagonalisation is quite scarce. This is why **approximate methods** such as the perturbation theory presented in the previous lecture are so hugely important in quantum mechanics. Here we are going to present another of these approximate methods, known as the variational principle. The main idea is to find some test wave function that provides an **upper bound** to the energy of the **ground state** of the system. By means of a clever choice of this test wave function, together with an optimisation of its adjustable parameters, we can obtain a very decent estimate of the ground state energy and wave functions of relatively complex systems without the need to solve the problem exactly.

5.1 Theoretical foundations

The key result underlying the variational principle method is the following. We would to determine the **ground state** of a given Hamiltonian \hat{H} , but are unable to solve its eigenvalue equation exactly for the ground state (or for any other state in general):

$$\hat{H}|\psi_{\text{gs}}\rangle = E_{\text{gs}}|\psi_{\text{gs}}\rangle. \quad (5.1)$$

Else we need to resort to some approximate method to estimate the ground state energy E_{gs} of this quantum system. We can demonstrate that if we select at random some **normalised state vector** $|\psi\rangle$, then we can obtain an **upper bound** on the ground state energy by evaluating the following matrix element:

$$E_{\text{gs}} \leq \langle \psi | \hat{H} | \psi \rangle = \langle H \rangle, \quad (5.2)$$

where the equality is only true if we use $|\psi_{\text{gs}}\rangle$ as our test function (at least, assuming that the ground state of our Hamiltonian is non-degenerate). In other words, the **expectation value** of the Hamiltonian of the system on some test function is guaranteed to provide an upper bound on E_{gs} . This result is of course trivial if $|\psi\rangle$ is one of the excited states of the Hamiltonian, but perhaps less so if this state vector has been genuinely chosen at random¹⁵

Let us demonstrate that this result is indeed true. To show this, I will express my **test state** $|\psi\rangle$ as a linear combination of the eigenvectors of my Hamiltonian, that is

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle \quad \text{where} \quad \hat{H}|\psi_n\rangle = E_n |\psi_n\rangle, \quad (5.3)$$

where as usual $\sum_n |c_n|^2 = 1$ due to the normalisation of the state vector, and the coefficients are computed as $c_n = \langle \psi_n | \psi \rangle$. I can now use this expansion to evaluate the expectation value of the Hamiltonian in the test state vector $|\psi\rangle$ as follows:

$$\langle \psi | \hat{H} | \psi \rangle = \sum_{n,m} c_n^* c_m \langle \psi_m | \hat{H} | \psi_n \rangle = \sum_{n,m} c_n^* c_m E_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2 E_n. \quad (5.4)$$

Again, this is what we expect: $\langle \psi | \hat{H} | \psi \rangle$ is nothing but the expectation value of the energy in our state $|\psi\rangle$. However, the ground state energy is by definition the **lowest of the energy eigenvalues** E_n , and hence

$$\langle \psi | \hat{H} | \psi \rangle = \sum_n |c_n|^2 E_n \geq \sum_n |c_n|^2 E_{\text{gs}} = E_{\text{gs}}, \quad (5.5)$$

¹⁵In practical applications, as we will show, a clever choice of the test function improves significantly the accuracy of our bound state energy estimate.

thus demonstrating the main result of the variational principle.

As you might have guessed, clever choices of the test state vector will provide much better estimates to E_{gs} than genuinely random choices.

Why variational?

The name of Variational Principle stems from the fact that in general our test state $|\psi\rangle$ will be made to depend on some **tunable parameters**, that determine for example the shape of the wave function. Then, once $\langle\psi|\hat{H}\psi\rangle$ as been computed, we can optimise the result by minimising with respect to these tunable parameters, since any of their values is still providing an upper bound on E_{gs} . In other words, we will determine the **optimal variation** of the test function parameters to achieve the lowest possible value for $\langle H\rangle$ and hence the **best possible estimate** for E_{gs} .

The variational method for the quantum harmonic oscillator. Let us now demonstrate how this method works for one specific quantum state for which we know the exact solution, and hence we can check whether or not the estimate provided by the variational principle is reasonable. Let's consider the **quantum harmonic oscillator** and try a Gaussian test function

$$\psi(x, b) = Ae^{-bx^2}, \quad (5.6)$$

where A is determined by normalisation and b is some positive real constant, which plays the role of adjustable parameter in our test function. You can check that $A = (2b/\pi)^{1/4}$ by evaluating the usual definite Gaussian integral, so b is the only genuine **free parameter** of our test function for the ground state of the system.

Following now the prescription provided by the **variational principle**, we need to take the Hamiltonian associated to this system

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d}{dx^2} + \frac{1}{2}m\omega^2 x^2, \quad (5.7)$$

and then compute its expectation value in the trial state defined in Eq. (5.13). We can evaluate separately the contributions from the kinetic and from the potential energy and find:

$$\langle T \rangle = -\frac{\hbar^2}{2m} \left(\frac{2b}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-bx^2} \left(\frac{d^2}{dx^2} e^{-bx^2}\right) = \frac{\hbar^2 b}{2m}, \quad (5.8)$$

$$\langle V \rangle = \frac{1}{2}m\omega^2 \left(\frac{2b}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx e^{-bx^2} (x^2 e^{-bx^2}) = \frac{m\omega^2}{8b}, \quad (5.9)$$

and combining the two contributions we find that an **upper limit** to the energy of the ground state of the harmonic operator Hamiltonian is given by

$$\langle H \rangle (b) = \left(\frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}\right) \geq E_{\text{gs}}. \quad (5.10)$$

Now, a crucial observation is that this result holds true for **any value of the free parameter** b , and hence the best estimate that we can have for the ground state energy is obtained by **minimizing** this expectation value of \hat{H} with respect to the value of b :

$$\frac{d\langle H \rangle (b)}{db} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \quad \rightarrow \quad b = \frac{m\omega}{2\hbar}. \quad (5.11)$$

We can now collect our results: our best estimate for the wave function and energy of the ground state of the quantum harmonic oscillator and its energy obtained by virtue of the variational principle (that is, we did not have to solve any differential equation!) will be

$$\psi(x) = \left(\frac{2b}{\pi}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right), \quad E_{\text{gs}} \leq \frac{1}{2}\hbar\omega. \quad (5.12)$$

By comparing with the **exact solution** for the ground state wave function of the harmonic oscillator, we see that in this case the equality is satisfied and the resulting wave functions and energies are **identical** to those of the exact result. This is no coincidence, since we have chosen a test function which is Gaussian, which is the same as in the exact solution. If you would have tried a different test function, such as for example

$$\psi(x, b) = Ae^{-b|x|}, \quad (5.13)$$

we would not have saturated the upper bound on E_{gs} , as you can check explicitly.

Choosing the test function

As we have seen from this example, the closer our test function $|\psi\rangle$ is to the actual ground state of the system $|\psi_{\text{gs}}\rangle$, the better the estimate provided by the variational principle will be. Actually, if you choose a functional form which is consistent with $\psi_{\text{gs}}(x)$ and then adjust the tunable parameters, you are **guaranteed** to recover the exact result for the ground state wave function $\psi_{\text{gs}}(x)$ and the energy E_{gs} **without having to solve the Schrodinger equation**.

The variational principle for the infinite square well. Another illustrative example of the usefulness of the variational principle is to deploy it to estimate the ground state wave function and energies of the infinite square well potential (again, we know the exact results for this quantum system, so this facilitates the validation of the method).

In this case the exact ground state energy and wave function are

$$E_{\text{gs}} = \frac{\hbar^2\pi^2}{2ma^2}, \quad \psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right). \quad (5.14)$$

Let us see how well we can approximate the ground state energy by using a test wave function which is **not sinusoidal** (hence we will not recover this time the exact value of E_{gs}). Since we know that the wave function must vanish at the edges of the potential well due to the wave function continuity, a possible choice for our test function will be

$$\psi(x) = \frac{2}{a}\sqrt{\frac{3}{a}}x \quad \text{for } 0 \leq x \leq a/2 \quad (5.15)$$

$$\psi(x) = \frac{2}{a}\sqrt{\frac{3}{a}}(a-x) \quad \text{for } a/2 \leq x \leq a \quad (5.16)$$

$$\psi(x) = 0 \quad \text{otherwise} \quad (5.17)$$

where the overall factor has been fixed by imposing the normalisation of the test wave function. Note that this function does not have any adjustable parameters, as opposed to the previous example¹⁶

¹⁶One option to improve this test wave function is to have that $\psi(x, p) \propto x^p ((1-x)^p)$ and then optimise the estimate with respect to the tunable parameter p .

We can now compute the expectation value of \hat{H} in this test wave function, which is reduced to the contribution of the **kinetic energy** inside the potential well (since the potential vanishes inside the well, and the wave function vanishes outside the well). We have to be careful here, since the test function $\psi(x)$ has a discontinuous first derivative, and hence its second derivative is expressed in terms of the Dirac delta function:

$$\frac{d^2\psi(x)}{dx^2} = \frac{2}{a}\sqrt{\frac{3}{a}}[\delta(x) - 2\delta(x - a/2) + \delta(x - a)]. \quad (5.18)$$

Equipped with this result, I can now evaluate the required value of the expectation value of the Hamiltonian,

$$\langle H \rangle = -\frac{\hbar^2}{2m} \int_0^a dx \psi(x) \frac{d^2\psi(x)}{dx^2} = \frac{12\hbar^2}{2ma^2}, \quad (5.19)$$

where the only delta function that contributes to the integral is the one at $x = a/2$. Hence our **upper bound to the ground state energy** for the infinite square well potential found with the variational principle is

$$\langle H \rangle = \frac{12\hbar^2}{2ma^2} \geq E_{gs} = \frac{\hbar^2\pi^2}{2ma^2} \quad (5.20)$$

which is quite a decent approximation, with the variational principle estimate giving a value 17% higher than the actual result. We could have improved our estimate by having the slope of the test function a free parameter and then minimise $\langle H \rangle$ with respect to it, or by trying polynomial test wave functions that resemble the sinusoidal behaviour of the exact ground state.

5.2 The ground state of Helium

The two previous examples have been discussed with a purely pedagogical motivation, since we knew the exact results of the corresponding Hamiltonians. We are now going to use the variational principle to obtain a **genuinely new result**, namely the ground state and energy of the **Helium atom** taking into account the electron repulsion. As we discussed in Sect. 3.2, the Schroedinger equation for the Helium atom cannot be solved exactly and it is thus mandatory to introduce some approximations.

Our starting point is the full Hamiltonian of the helium atom

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right). \quad (5.21)$$

Previously, we found a solution for the ground state and energy by **neglecting the electron repulsion term**, which we then improved phenomenologically using the idea of effective electric charge. Let us now use the variational principle to determine an alternative estimate of the ground state wave function which takes into account from the very beginning the electron repulsion.

As a **test function**, we will use the following function:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}, \quad (5.22)$$

which is the solution for the ground state of the Helium atom assuming that the electrons are **non-interacting**, that is, when the electron repulsion is neglected. This choice is convenient because it is an eigenfunction of the Hamiltonian of the system minus the electron repulsion term, that is,

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle \quad (5.23)$$

where $E_1 = -13.6$ eV is the **ionisation energy** of the hydrogen atom, and the factor 8 comes because the energies of hydrogen-like atoms scale as $E_n^{(Z)} = Z^2 E_n^{(H)}$ in terms of the hydrogen atom energies.

The expectation value of the electronic repulsion potential is given by

$$\langle V_{ee} \rangle \equiv \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left(\frac{8}{\pi a^3} \right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-4(r_1+r_2)/a} \quad (5.24)$$

If we are able to evaluate this integral, we will obtain the variational principle estimate for the ground state of the helium atom. The evaluation of the integral is presented in the textbook, and here we just quote its result

$$\langle V_{ee} \rangle = -\frac{5}{2} E_1 \simeq 34 \text{ eV}, \quad (5.25)$$

and hence we find that the variational principle tells us that an upper bound for the ground state energy of the Helium atom will be given by:

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle = -75 \text{ eV} \geq E_{\text{gs}}. \quad (5.26)$$

If we compare with the experimental result, $E_{\text{gs}} = -78.975$ eV, we can observe that the estimate provided by the variational principle is much better than the one provided by neglecting the inter-electron repulsion, $8E_1 = -109$ eV. So this is a nice result, specially since we could **recycle** a known wave function which was already eigenfunction of most of the Hamiltonian to reduce the computational burden of the problem.

We have seen from our previous examples that it is convenient to endow our test wave function with some **free parameter** and then minimise the value of $\langle H \rangle$ with respect to it. This way we can further improve our estimate for E_{gs} for the Helium atom. In Sect. 3.2 we introduced the idea of the **effective charge** to partially account for the screening that the electrons induce in the total positive charge of the helium nucleus. There the value of Z_{eff} was fixed by some phenomenological analysis to reproduce the experimental results, here we will determine this effective charge from **first principles** using the variational method.

With this motivation, instead of the parameter-free test function Eq. (5.22) that we used before, we will adopt now the following test function

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2, Z) = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}, \quad (5.27)$$

with Z being a free parameter to be optimised once we have evaluated the expectation value $\langle H \rangle$. It is clear that the result of this calculation will then be the **optimal value of the effective electric charge** which accounts for the electron repulsion. Let us now apply the variational principle to this system.

This wave function is an eigenstate of the “unperturbed” Hamiltonian (neglecting the electron repulsion) if it had Z in the Coulomb terms rather than 2. To account for this property, we rewrite Eq. (5.21) as follows:

$$\begin{aligned} H &= -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \\ &+ \frac{e^2}{4\pi\epsilon_0} \left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right). \end{aligned} \quad (5.28)$$

Hence, the expectation value of Eq. (5.21) using the test wave function Eq. (5.27) will be given by

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2) \left\langle \frac{e^2}{4\pi\epsilon_0} \right\rangle \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle, \quad (5.29)$$

where the expectation value of r^{-1} is computed using the ground state wave function of a hydrogen-like atom with electric charge Z :

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a}. \quad (5.30)$$

For the average of V_{ee} we also need to account for the new electric charge factor Z ,

$$\langle V_{ee} \rangle = -\frac{5Z}{2} E_1, \quad (5.31)$$

and hence our final result for the expectation value of the (full) Hamiltonian of the Helium atom in the test wave function Eq. (5.27) will be given by

$$\langle H \rangle = [-2Z^2 + (27/4)Z] E_1. \quad (5.32)$$

The final step of the variational principle calculation is to optimise this result with respect to the value of the adjustable parameter Z , namely

$$\frac{d\langle H \rangle}{dZ} = [-4Z + (27/4)] E_1 = 0 \quad (5.33)$$

which leads to a **first principle calculation of the effective charge** of the Helium atom in the ground state, whose value is given by

$$Z = \frac{27}{16} = 1.69, \quad (5.34)$$

which is in good agreement with the phenomenological result, and that leads to an expectation value of

$$\langle H \rangle = -77.5 \text{ eV}, \quad (5.35)$$

which is now really close to the experimentally measured value of $E_{\text{gs}} = -78.975 \text{ eV}$. As expected, the addition of a tunable parameter to the test wave function has led to an improved estimate of the ground state energy as compared to the parameter-less test function Eq. (5.22).

This calculation demonstrates the usefulness and reliability of the variational method to estimate the ground state wave functions and energies of complex quantum systems for which the exact solutions are not available. By trying **more flexible test functions** and a **higher number of tunable parameters**, one can achieve each time more precise estimates of the value of E_{gs} in a systematic manner.

Summary

We can now recapitulate what have we learned in this chapter concerning the use of the variational principle to determine approximations to the energies and the wave functions of the ground states of quantum systems that cannot be solved exactly.

- I/ The variational principle procedure guarantees an **upper bound** on the ground state of a general Hamiltonian, no matter how complex this is.
- II/ By using test functions with more or one **tunable parameters**, we can improve in a systematic manner this estimate of the ground state energy.
- III/ If we use a test function which has the same functional dependence of the exact ground state with an approximate number of tunable parameters, the variational principle calculation will return the **exact wave function and ground state energy** E_{gs} without having to solve the Schroedinger question.

IV/ By means of the variational principle, we can construct an approximation to the **ground state of the Helium atom** which is in very good agreement with the experimental data and carry out a **first principle calculations of the effective charge** accounting for the effects of electron repulsion in the system.