Lecture 21 & 22

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In the last two lectures, we have discussed the formalism for time-independent perturbation theory, both in the degenerate and non-degenerate cases. In this lecture, we will discuss different applications of this formalism.

First, let us begin with non-degenerate perturbation theory. In this case, we consider the Hamiltonian

$$H = H_0 + \lambda V \tag{1}$$

where H_0 is assumed to be exactly solvable with eigenstates $|n^{(0)}\rangle$ and eigenenergies $E_n^{(0)}$, $H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$. The eigenstates and eigenenergies of the full Hamiltonian are expressed as a series expansion in λ via

$$|n\rangle = \sum_d \lambda^d |n^{(d)}\rangle, \qquad E_n = \sum_d \lambda^d E_n^{(d)} \tag{2}$$

Last week, we derived expressions for the leading terms in the perturbative expansion:

$$E_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle, \qquad E_n^{(2)} = \sum_{k\neq n} \frac{|\langle k^{(0)}|V|n^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}} \tag{3}$$

$$|n^{(1)}\rangle = \sum_{k\neq n} |k^{(0)}\rangle \frac{\langle k^{(0)}|V|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} \tag{4}$$

We have also derived the following lower and upper bounds for the second order perturbative correction to the ground state energy

$$E_0^{(2)} = -|E_0^{(2)}|, \qquad |E_0^{(2)}| = \sum_{k\neq 0} \frac{|\langle k|V|0\rangle|^2}{\Delta_k}, \qquad \Delta_k = E_k - E_0 \tag{5}$$

given by

$$\frac{|\langle 1|V|0\rangle|^2}{\Delta_{\min}} \leq |E_0^{(2)}| \leq \frac{\langle 0|V^2|0\rangle - |\langle 0|V|0\rangle|^2}{\Delta_{\min}} \tag{6}$$

Historically, the earliest and most prominent application of perturbation theory was to understand the fine features of the atomic spectra with the simplest example being the Hydrogen atom. For an energy level with principal quantum number n, we have found earlier that the degeneracy of the energy levels is n^2 (ignoring spin). This means that for $n > 1$, understanding the effect of any perturbation requires the use of non-degenerate perturbation theory. On the other hand, for $n = 1$ and for spin-independent perturbations, we can use the non-degenerate perturbation theory described above. A simple and illustrative example is the (quadratic) Stark effect.

The Stark effect corresponds to the shift in the energy levels in the presence of an electric field. It is obtained by considering the Hamiltonian (1) with

$$H_0 = H_{\text{Hydrogen}}, \qquad V = -eEz, \qquad e < 0 \tag{7}$$

Here, we assumed the magnetic field is in the z direction, $\boldsymbol{E} = E\hat{z}$. We will consider the limit of small E so that the perturbation V can be considered small [1].

The effect of the perturbation V on the energy of the lowest energy state $n = 1$ in the Hydrogen atom, labelled $|1, 0, 0\rangle$ ($n = 1$, $l = 0$, $m = 0$) can be understood as follows. First, we notice that the first order contribution to the energy vanishes since $\langle 1, 0, 0|z|1, 0, 0\rangle = 0$. This can be understood by recalling that the spherical harmonic $Y^{l=0}_{m=0}$ is spherically symmetric (it is independent of the angles θ and φ), so the angular integral $\int d\theta \sin\theta \cos\theta |Y^0_0|$ vanishes. Another way to see this is using the parity selection rule we discussed earlier. Since H_0 is parity symmetric, a non-degenerate eigenstate has to be a parity eigenvalue, but since V is odd under parity, then its expectation value in any parity eigenstate has to vanish since $\langle 1, 0, 0|V|1, 0, 0\rangle = \langle 1, 0, 0|\pi V \pi|1, 0, 0\rangle = -\langle 1, 0, 0|V|1, 0, 0\rangle = 0$.

This means that the leading contribution to the energy of the $n = 1$ state is quadratic in E. It is given by

$$E^{(2)}_0 = -\frac{1}{2}\alpha E^2, \qquad \alpha = 2e^2 \sum_{k \neq (1,0,0)} \frac{|\langle k|z|1, 0, 0\rangle|^2}{E_k - E_{1,0,0}} \tag{8}$$

Notice here that the sum does not only include the bound states of the Hydrogen atom but also the extended (scattering) states that we have not discussed. Evaluating this expression is quite tedious but can be done analytically yielding the result $\alpha = 4.5a^3_0$.

Let us now see what we get from the bounds (6). The lower bound can be evaluated by computing the matrix elements of z between the ground state with principal quantum number $n = 1$ and the first excited states with $n = 2$. There are 4 such states with $l = 0, m = 0$ or $l = 0, m = -1, 0, +1$. We will now show that some of the matrix elements between $|1, 0, 0\rangle$ and these states vanish by symmetry. We begin by noting that the electric field along the z-direction breaks full rotation symmetry but still retains a 2D subgroup corresponding to rotations around the z-axis. This means that $[V, \boldsymbol{L}^2] \neq 0$ but $[V, L_z] = 0$. As a result, the matrix elements of V between states with different m should still vanish since

$$0 = \langle l, m|[L_z, V]|l', m'\rangle = \hbar(m - m')\langle l, m|V|l', m'\rangle \tag{9}$$

Thus, for $m \neq m'$, $\langle l, m|V|l', m'\rangle$ has to vanish. This means that we can only have non-vanishing matrix elements between the states $|1, 0, 0\rangle$ and $|2, 0\rangle$ or $|2, 1, 0\rangle$. Furthermore, since the $|l, m\rangle$ states are parity eigenstates, and the electric field is odd under parity, it can only connect states with opposite parity. Using the fact that that s-orbitals ($l = 0$) have even parity whereas p-orbitals ($l = 1$) have odd parity, we see that the only non-vanishing matrix elements of z is between $|1, 0, 0\rangle$ and $|2, 1, 0\rangle$. We can compute this directly to get

$$\langle 1, 0, 0|z|2, 1, 0\rangle \approx 0.745a_0 \tag{10}$$

Using $\Delta E_{\min} = \frac{e^2}{2a_0}[1 - \frac{1}{4}] = \frac{3e^2}{8a_0}$, this leads to the lower bound

$$\alpha \geq 2.96a^3_0 \tag{11}$$

We can similarly derive an upper bound following Eq. 6

$$\alpha \leq \frac{16a_0}{3}\langle z^2\rangle \tag{12}$$

where we used the shorthand $\langle z^2\rangle$ for $\langle 1, 0, 0|z^2|1, 0, 0\rangle$. Due to the full rotation symmetry of the $n = 1$ state, $\langle z^2\rangle = \langle x^2\rangle = \langle y^2\rangle = \frac{1}{3}\langle r^2\rangle$. Recalling that the radial part of the Hydrogen atom wavefunction goes as e^{-r/a_0}, we find

$$\langle r^2\rangle = \frac{\int_0^\infty dr r^4 e^{-2r/a_0}}{\int_0^\infty dr r^2 e^{-2r/a_0}} = 3a^2_0 \tag{13}$$

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[1] An important subtlety here is that since the potential V is unbounded from below (it goes to $-\infty$ at $z \to -\infty$), perturbation theory is strictly speaking not applicable. In particular, bound states can now escape. However, for small V, the lifetimes of such bound states will be long so that it still makes sense to talk about the energies of the states as long lived metastable states.

which implies $\langle z^2 \rangle = a_0^2$. Substituting in (12) gives

$$\alpha \leq \frac{16a_0^3}{3} = 5.3a_0^3 \tag{14}$$

We see that this upper bound is not so far off the actual value. The reason for this is the following. Since the energy goes as $1/n^2$ for the bound states, the recplacement of the denominator by ΔE only introduces a small error for $n > 2$. For the extended states, this replacement may introduce large errors since the denominator is unbounded but the matrix elements $|\langle k|z|1,0,0\rangle|$ are expected to be small since they include the overlap between a bound state whose probability is concentrated over a small region in space and a plane wave whose probability to be in this region is very small.

To understand the effect of electric field on higher energy levels, we need to employ degenerate perturbation theory. As we discussed last time, in degenerate perturbation theory we consider certain subspaces labelled by $|n^{(0)}, l\rangle$ where l labels the states within each subspace. Each subspace is characterized by small energy separation between the states when the energy is evaluated using the unperturbed Hamiltonian H_0. In degenerate perturbation theory, the action of the perturbation is assumed to modify the degenerate subspaces labelled by n only perturbatively, whereas its effect on the individual states within each subspace could be large. This is captured by writing an effective Hamiltonian

$$H|n,l\rangle = h_{n,ll'}|n,l'\rangle \tag{15}$$

where $|n,l\rangle$ and $h_{n,ll'}$ have the perturbative expansions

$$h_n = \sum_d \lambda^d h_n^{(d)}, \qquad |n,l\rangle = \sum_d \lambda^d |n^{(d)}, l\rangle \tag{16}$$

The generalization for the expression (3) to the degenerate case is given by

$$h_{n,ll'}^{(1)} = \langle n^{(0)}, l'|V|n^{(0)}, l\rangle, \qquad h_{n,ll'}^{(2)} = \sum_{k\neq n} \frac{\langle n,l|V|k^{(0)}\rangle\langle k^{(0)}|V|n,l'\rangle}{E_{nl}^{(0)} - E_k^{(0)}} \tag{17}$$

We would now like to use this formalism to understand the effect of electric field, Eq. 7, on the energy levels of the Hydrogen atom for $n > 1$. For simplicity, let us consider the case $n = 2$. Here, we have 4 degenerate eigenstates corresponding to $l = 0, m = 0$ (2s orbital) and $l = 1$, $m = 0, \pm 1$ (2p orbitals). Similar to our earlier discussion, we use the fact that the field in the z-direction breaks the full rotation symmetry but retains rotation symmetry about the z-axis to conclude that we can only have non-vanishing matrix elements between the states $|0,0\rangle$ and $|1,0\rangle$. Furthermore, since the $|l,m\rangle$ states are parity eigenstates, the diagonal matrix elements $\langle l,m|V|l,m\rangle$ are also zero. This means that the matrix h has the form

$$h = \begin{pmatrix} 0 & \langle 0,0|V|1,0\rangle & 0 & 0 \\ \langle 1,0|V|0,0\rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{18}$$

where the basis states are $|0,0\rangle$, $|1,0\rangle$, $|1,1\rangle$, and $|1,-1\rangle$. The matrix element $\langle 0,0|V|1,0\rangle$ can be directly evaluated as $3ea_0E$. Thus, the first order correction to the energy

$$\Delta_{\pm}^{(1)} = \pm 3ea_0 E \tag{19}$$

The corresponding energy eigenstates are

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|0,0\rangle \pm |1,0\rangle) \tag{20}$$

Notice that the effect of electric field in degenerate perturbation theory is linear rather than quadratic. This can be understood by noting that, in the absence of degeneracy, all eigenstates are parity eigenstates so the eigenstates can have no dipole moment which leads to the vanishing of the linear term in perturbation theory. The only response to electric field is then obtained through the quadratic (polarizability term) which can be understood as a field-induced dipole moment. On the other hand, in the degenerate case, we can choose linear combinations of the states which have a dipole moment and such combinations acquire linear energy corrections proportional to their dipole moment in the presence of field.

The final effect we would like to discuss is the spin-orbit coupling. Spin-orbit coupling is ultimatley a relativistic effect so its proper treatment should wait until we introduce the proper relativistic generalization of quantum mechanics, the Dirac equation. Here, I will instead present a crude intuitive argument that turns out to reproduce the correct expression up to a factor of 2. The idea is that an electron moving in any potential feels an electric field given by

$$\boldsymbol{E} = -\frac{1}{e}\nabla V \tag{21}$$

For the particular case where the potential only depends on the radial coordinate, we get an electric field pointing in the radial direction given by

$$\boldsymbol{E} = -\frac{1}{e}\frac{\boldsymbol{r}}{r}\frac{d}{dr}V(r) \tag{22}$$

Now, although in the rest frame of the nucleus, there is no magnetic field, in the rest frame of the electron it feels an effective magnetic field since it sees the nucleous moving with velocity $-\boldsymbol{v}$ [2]. The effective magnetic field is given by

$$\boldsymbol{B}_{\text{eff}} = -\frac{1}{c^2}\boldsymbol{v}\times\boldsymbol{E} = -\frac{1}{mc^2}\boldsymbol{p}\times\boldsymbol{E} \tag{23}$$

Substituting (22) in (23) yields

$$\boldsymbol{B}_{\text{eff}} = -\frac{1}{mc^2 er}\frac{d}{dr}V(r)\boldsymbol{L} \tag{24}$$

Thus, there is an effective magnetic field that is proportional to the orbital angular momentum. On the other hand, since the electron has a magnetic moment proportional to its spin, its energy in the presence of a field is changed by

$$\Delta H_{\boldsymbol{B}} = -\boldsymbol{\mu}\cdot\boldsymbol{B}, \qquad \boldsymbol{\mu} = \frac{e\boldsymbol{S}}{mc} \tag{25}$$

Thus, there is a correction to the Hamiltonian due to the effective magnetic field given by

$$\Delta H_{LS} = \frac{1}{m^2c^2 r}\frac{d}{dr}V(r)\boldsymbol{L}\cdot\boldsymbol{S} \tag{26}$$

The actual correct answer turns out to be smaller by a factor of 2

$$\Delta H_{LS} = \frac{1}{2m^2c^2 r}\frac{d}{dr}V(r)\boldsymbol{L}\cdot\boldsymbol{S} \tag{27}$$

Applying degenerate perturbation theory we see that this term can lead to linear corrections to the energies within the $2n^2$ degenerate subspace for a given principal quantum number n. This degenerate subspace is labelled by the the eigenvalues of $\boldsymbol{L}^2$, L_z, $\boldsymbol{S}^2$, S_z corresponding to the quantum numbers l, m, $s = 1/2$, and $m_s = \pm 1/2$. The spin orbit coupling term commutes with $\boldsymbol{S}^2$ and $\boldsymbol{L}^2$ but not with L_z and S_z. We can compute the matrix elements of ΔH_{LS} between states with different m and m_s, but a much more convenient approach is to use the formalism for the addition of angular momentum we developed earlier. We can introduce the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ and notice that $2\boldsymbol{L}\cdot\boldsymbol{S} = \boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2$ which implies that $\boldsymbol{L}\cdot\boldsymbol{S}$ commutes with both $\boldsymbol{J}^2$ and J_z. This means that we can label the states with the quantum numbers l, s, j and m_j instead of l, s, m, and m_s. In the new basis, ΔH_{LS} is diagonal and we only need to compute the

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[2] We are here neglecting for the moment that this is not an inertial frame

diagonal matrix elements. The transformation between the two basis is performed via the Clebsch-Gordan coefficients we discussed earlier.

We now notice that the action of $\boldsymbol{L}\cdot\boldsymbol{S}$ is simple in the new basis since

$$\boldsymbol{L}\cdot\boldsymbol{S}|l,s,j,m_j\rangle = \frac{1}{2}(\boldsymbol{J}^2-\boldsymbol{L}^2-\boldsymbol{S}^2)|l,s,j,m_j\rangle = \frac{\hbar^2}{2}(j(j+1)-l(l+1)-s(s+1))|l,s,j,m_j\rangle \tag{28}$$

We can substitute $s = 1/2$ above. The first order energy correction is diagonal in the new basis and given by

$$\Delta_{l,j,m_j} = \langle\frac{1}{2m^2c^2r}\frac{d}{dr}V(r)\rangle_{n,l,j,m_j}\frac{\hbar^2}{2}(j(j+1)-l(l+1)-\frac{3}{4}) \tag{29}$$

For Coulomb potential with atomic number Z, we have $V(r) = -\frac{Ze^2}{r}$. Thus, we need to evaluate the expectation value $\langle\frac{Ze^2}{r^3}\rangle_{n,l,j,m_j}$. While we can try doing this by brute force, there is a nice trick we can use. First, we notice that since the states $|n,l,j,m_j\rangle$ are eigenstates of the Hamiltonian, the expectation value of the commutator $\langle[H_0,A]\rangle_{n,l,j,m_j}$ vanishes for any operator A where $H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{\hbar^2 l(l+1)}{2mr^2}-\frac{Ze^2}{r}$ is the radial Hamiltonian. Now choosing $A = \frac{d}{dr}$, we get the identity

$$\langle\frac{1}{r^3}\rangle_{n,l,j,m_j} = \frac{2Ze^2m^2}{l(l+1)\hbar^4}\langle\frac{\hbar^2}{2mr^2}\rangle_{n,l,j,m_j} \tag{30}$$

The term $\frac{\epsilon\hbar^2}{2mr^2}$ effectively modifies the centrifugal term by sending $l \mapsto l+\frac{\epsilon}{2l+1}$, which correspond to a correction to the energy $\Delta E_n = E_{n+\frac{\epsilon}{2l+1}} - E_n = \frac{1}{2}mc^2\frac{Z^2\alpha^2}{n^3}\frac{\epsilon}{l+1/2} = -\frac{1}{n(l+1/2)}E_n$. This gives

$$\langle\frac{Ze^2}{r^3}\rangle = -\frac{2Z^2e^4m^2}{nl(l+1)(l+1/2)\hbar^4}E_n = -\frac{2Z^2\alpha^2m^2c^2}{nl(l+1)(l+1/2)\hbar^2}E_n \tag{31}$$

Substituting in the energy expression gives

$$\Delta_{n,l,j,m_j} = -\frac{Z^2\alpha^2}{nl(l+1)(l+1/2)}E_n(j(j+1)-l(l+1)-\frac{3}{4}) \tag{32}$$

The correction is proportional to the energy eigenvalue E_n times the dimensionless number $Z^2\alpha^2$ where α is the fine structure constant $\alpha = \frac{e^2}{\hbar c}\approx\frac{1}{137}$. The smallness of the fine structure constant justifies the perturbative treatment. An important observation is that the spin-orbit coupling scales as the square of the atomic number so it becomes more important for heavier elements.

1 Variational principle

In perturbation theory, we found that we can find approximate solutions to quantum mechanical problems which are sufficiently close to an exactly solvable limit. However, this is not always possible. In many cases, we want to solve a problem that is not close to a solvable limit or where perturbation theory is known to fail. In this case, another approximation approach, known as the variational principle, is very helpful.

The variational principle is mainly used to estimate the energy and the wavefunction for the ground state of a given Hamiltonian. It can be adapted in some cases to determine excitations but we will not consider such cases here. The variational principle relies on the simple observation that since the ground state is the lowest energy eigenstate of the Hamiltonian and since we can expand an arbitrary state in terms of eigenstates of the Hamiltonian (since they form a complete basis), then the expectation value of the Hamiltonian in *any* state has to be larger than or equal that in the ground state. To see this explicitly, consider a Hamiltonian H with eigenstates $|n\rangle$ and eigenenergies E_n, $n = 0,1,\dots$ with $E_0 \leq E_1 \leq E_2\dots$. For an arbitrary state $|\psi\rangle$, the energy expectation value is given by

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \tag{33}$$

Here, we have taken into account that $|\psi\rangle$ is not necessarily normalized. We can expand $|\psi\rangle$ in terms of the complete basis $|n\rangle$

$$|\psi\rangle = \sum_n c_n|n\rangle, \qquad c_n = \langle n|\psi\rangle \tag{34}$$

Substituting in (33), we get

$$E = \sum_n \frac{|c_n|^2 E_n}{\sum_m |c_m|^2} = \sum_n \frac{|c_n|^2(E_n - E_0 + E_0)}{\sum_m |c_m|^2} = E_0 + \sum_n \frac{|c_n|^2(E_n - E_0)}{\sum_m |c_m|^2} \geq E_0 \tag{35}$$

Thus, the energy expectation value of $|\psi\rangle$ provides an upper bound on the ground state energy. Furthermore, this bound is saturated if and only if $|c_n|^2(E_n - E_0) = 0$ which means that $|\psi\rangle$ is a ground state, $H|\psi\rangle = E_0|\psi\rangle$.

While the variational method does not provide us with a control to how close we are to the actual ground state, we can use our physical intuition about the problem to come up with some good guess for the ground state. Variational methods are particularly powerful if we can come up with a family of wavefunctions $|\psi_{\{\xi\}}\rangle$ parametrized by a family of parameters $\{\xi\}$ that we expect provides a good approximation for the ground state. We can then compute the variational energy as a function of $\{\xi\}$ and find the minimum of $E_{\{\xi\}}$. We expect that, at least within this family, this minimum value provides the best approximation of the ground state and if this family of states is chosen properly we usually get a good approximation for the ground state and its energy.

Let us now consider some examples. If we want to find the ground state for the 1D Schrödinger equation for a potential that grows at infinity or at least is sufficiently large such that we have a bound state, then we know the ground state does not have any zeros and that it has to decay at infinity. We can also impose further symmetry requirements. For instance, for parity-symmetric potentials, the ground state should have even parity. These considerations suggest using a Gaussian variational ansatz $\psi_\xi(x) = e^{-\frac{x^2}{2\xi^2}}$ labelled by a single positive real number ξ is a good starting point to estimate the ground state for a general potential that grows at $\pm\infty$. Let us first consider the Harmonic oscillator whose Hamiltonian is given by

$$H = \frac{1}{2}\hbar\omega\left[-\frac{d^2}{dx^2} + x^2\right] \tag{36}$$

Here, we are measuring x in terms of $l = \sqrt{\hbar/m\omega}$. The variational energy is given by

$$E_\xi = \frac{1}{2}\hbar\omega\epsilon_\xi, \qquad \epsilon_\xi = \frac{\int_{-\infty}^{\infty} dx\psi_\xi(x)H\psi_\xi(x)}{\int_{-\infty}^{\infty} dx\psi_\xi(x)\psi_\xi(x)} = \frac{1}{2\xi^2} + \frac{1}{2}\xi^2 \tag{37}$$

This expression grows at $\xi \to 0$ and $\xi \to \infty$ so it should have a minimum somewhere in between. To find the minimum, we simply set $0 = \frac{d\epsilon_\xi}{d\xi} = -\xi^{-3} + \xi$ which implies $\xi^4 = 1$ whose only real solution is $\xi = 1$. The corresponding dimensionless energy is $\epsilon_\xi = 1$. In the original dimensionful units, this corresponds to $\xi = l$ and $E = \frac{1}{2}\hbar\omega$. This is the same as the exact answer since the family of states ψ_ξ does contain the harmonic oscillator ground state.

Let us now consider another example. Consider the linear potential $V(x) = k|x|$. The Hamiltonian can be written in terms of a dimensionless position variable x measured in units of $x_0 = (\hbar^2/mk)^{1/3}$ and the energy scale $\varepsilon_0 = kx_0$ as

$$H = \varepsilon_0\left[-\frac{1}{2}\frac{d^2}{dx^2} + |x|\right] \tag{38}$$

We can now use the same variational state and write

$$E_\xi = \varepsilon_0\epsilon_\xi, \qquad \epsilon_\xi = \frac{\int_{-\infty}^{\infty} dx\psi_\xi(x)H\psi_\xi(x)}{\int_{-\infty}^{\infty} dx\psi_\xi(x)\psi_\xi(x)} = \frac{1}{4\xi^2} + \frac{1}{\sqrt{\pi}}\xi \tag{39}$$

This expression also grows at 0 and infinity and has a minimum between given by $0 = \frac{d\epsilon_\xi}{d\xi} = -\frac{1}{2}\xi^{-3} + \frac{1}{\sqrt{\pi}}$ whose only real solution is $\xi = (\sqrt{\pi}/2)^{1/3}$. The corresponding dimensionless energy is $\epsilon_{\min} = \frac{3}{2(2\pi)^{1/3}} \approx 0.813$. This potential can be exactly solved with wavefunctions that can be written in terms of Airy functions. The exact ground state energy $\epsilon \approx 0.809$. We see that the variational method provides an excellent approximation for the ground state energy since the difference between the variational and exact energies is $\approx 0.004 E_0$ where E_0 is the natural energy scale of the problem.

Let us consider a third example with a quartic potential

$$H = \varepsilon_0 \left[-\frac{1}{2}\frac{d^2}{dx^2} + x^4 \right] \tag{40}$$

This is a potential for which no analytical solution exists. However, we can still solve this equation numerically to find that the ground state energy is $\approx 0.668 E_0$. Using the Gaussian variational ansatz, we find

$$\epsilon_\xi = \frac{1}{4\xi^2} + \frac{3}{4}\xi^4 \tag{41}$$

Again this expression has at least one minimum for positive ξ obtained by solving $0 = \frac{d\epsilon_\xi}{d\xi} = -\frac{1}{2}\xi^{-3} + 3\xi^3$ leading to $\xi = 1/6^{1/6}$. The corresponding energy is $\epsilon_{\min} = \left(\frac{3}{4}\right)^{4/3} \approx 0.681$. We see again that the difference between the variational and exact solutions is very small $0.013 E_0$.

In all the examples we considered we found that the Gaussian ansatz provided a good approximation for the ground state energy. How about the ground state wavefunction? In general, a state which provides a good approximation to the ground state energy could have very little overlap with the actual ground state if it happened that there is another eigenstate of the Hamiltonian whose energy is close to the ground state [3] On the other hand, in many cases, we can place a lower bound on the gap between the ground state energy and that of excited states. If we know the gap to the first excited state is at least Δ, then we can use Eq. 35 to write (here for simplicity, we will assume $|\psi\rangle$ is normalized)

$$E - E_0 = \sum_n |c_n|^2 (E_n - E_0) \geq \Delta \sum_{n=1} |c_n|^2 = \Delta(1 - |c_0|^2) \tag{42}$$

This implies that the deviation of the wavefunction overlap from 1 cannot exceed $\frac{E-E_0}{\Delta}$ or equivalently

$$|\langle\psi|0\rangle| \geq \sqrt{1 - \frac{E - E_0}{\Delta}} \approx 1 - \frac{E - E_0}{2\Delta} \tag{43}$$

In all the 1D cases we considered, since we have a confining potential, we expect the spacing between eigenstates to be of order E_0 where E_0 is the typical energy scale of the problem. Thus, since the difference $E - E_0$ was at most 1%, we expect a very large overlap $> 99\%$ with the actual ground state wavefunction.

As a final example for the variational method, we consider the problem of the ground state of the Helium atom. Here, we have two electrons and two protons. The Hamiltonian takes the form

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{44}$$

Without the last term, this Hamiltonian simply decomposes into a sum of Hamiltonians for the first and the second electrons whose ground state can be obtained by separation of variables to be the product of ground states of each Hamiltonian separately $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2)$. However, the last term makes it impossible to perform a separation of variables. Note that there is no sense in which the last term is a small

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[3] An extreme case would be if the first excited state has energy very close to the ground state and our variational ansatz happens to be exactly equal to that state. In this case, the ansatz will have zero overlap with the ground state due to the orthogonality of different wavefunctions.

perturbation to the problem since it is of the same order as the interaction between each of the electrons and the nucleus, so we do not expect perturbation theory to be applicable.

So How do we proceed? we can begin by deriving a crude bound where we simply use the state

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2) = e^{-2(r_1+r_2)/a_0} \tag{45}$$

as an ansatz. Recall that the ground state energy of a single-particle in the Coulomb potential $V(r) = -\frac{Ze^2}{r}$ is $-Z^2 R_y$ where $R_y = 13.6$ eV. Thus, the energy expectation value for the two electrons excluding the last (electron-electron interaction) term is $-8R_y \approx -109$ eV. The expectation value of the last term can be evaluated as $5R_y/2 \approx 34$ eV, leading to the variational energy estimate -75 eV. The actual energy measured experimentally or determined using more sophisticated methods is -78.96 eV which means that our variational estimate is off by 3.96eV which is around 5% error. Is there a way to do a better variational estimate? it turns out there is. This comes from the observation that for each electron, the presence of the other electrons means that on average it sees a reduced nuclear charge. This can be implemented by assuming the wavefunction is again a product of two separate ground state wavefunctions for a Coulomb potential but with a reduced value of Z. Such ansatz can be written explicitly as

$$\psi_Z(\boldsymbol{r}_1, \boldsymbol{r}_2) = e^{-Z(r_1+r_2)/a_0} \tag{46}$$

The variational energy is then given by

$$E_Z = R_y \left[2Z^2 - \frac{27}{4}Z\right] \tag{47}$$

This expression has a minimum at $Z = 27/16 \approx 1.69$ with minimum energy $E = -77.5$ eV. We see that this gives a better estimate of the total energy since the energy difference is now 1.46 which is within 2% of the actual value. The value of $Z \approx 1.69$ can be physically interpreted as each electron seeing an effective nuclear charge reduced by roughly $0.3e$ due to the other electron.

This example is an illustration of a powerful set of methods known as mean-field or Hartree-Fock methods where we write a variational ansatz for the ground state of many-interacting electrons in terms of a product of single-particle states that depends on some physically motivated variational parameters. More sophisticated variational methods employing more complicated wavefunctions are also used (e.g. Density matrix renormalization group which uses variational states called tensor networks or matrix product states) and is an active area of research.