

Lecture 7: Quantum Mechanics

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A. Variational Approximation in Physics (by Oleg)

Numerous main principles in physics are stated as minimization problems of some multiple parameter function or of some functional (which is just a continuous generalization of multiple parameter functions). The examples are minimal action principle in mechanics, minimization of the relevant thermodynamic potential in Statistical Physics, Fermat's principle in optics etc. This is no surprise since the physical world picks some particular way to behave (a solution) under the given constraints, and we construct our math to phrase this particularity as a minimum of some functional.

Let's say we are minimizing some functional over the space of some continuous functions. Normally, we should consider the whole space and the minimum we find through variation will be the true solution of the problem. The point of the variational *approximation* is to instead consider a very limited set of functions, that are parametrized by a few or even a single parameter(s). Then the variational minimization is reduced to finding the minimum of the functional with respect to these parameter(s). If the shape of the functions is chosen with the understanding of physical principles behind the phenomenon, the obtained results should provide a fair estimate of the correct values. One can further improve on the results by introducing more parameters into the search functions set.

Let's consider two examples of the use of variational approximation and then we will apply this method to the structure of atoms.

1. Atmosphere height

We will consider the density distribution in isothermic atmosphere, i.e. (with constant temperature T). For simplicity we will assume that the atmosphere contains a single specie of molecules, say N_2 . Generally speaking, for an exact solution we should be minimizing the free energy functional $F[n(z)]$ of air density profiles $n(z)$ under the constraint of constant number of particles. This approach eventually leads to the understanding that the chemical potentials at each level should be the same, which in turn leads to the exponentially decaying density profile with the characteristic decay length of $H^* = k_B T / mg$.

Let's say we are interested in a rough estimation of the atmosphere height. We could simplify the calculation through the variational estimation, by considering density profiles parametrized with a single parameter. To suggest the profile shape we have to consider the physical principles first. Here we have a competition between the two terms of the free energy $F = U - k_bTS$: the energy term favours molecules sitting on the Earth surface, while the entropy term would send them freely floating in space. The minimum of F is reached by some kind of a compromise between the two terms: the molecules find themselves within some distance from Earth, not too close to have some entropy and not too far to lower their potential energy. This type of solution can be captured by, e.g. step like profile:

$$n = \begin{cases} n_0, & \text{for } z < H \\ 0, & \text{for } z > H \end{cases} \quad (1)$$

Instead of minimizing F using variations with respect to huge set of possible $n(z)$ functions we will be minimizing F with respect to a single parameter H that defines our density profile. Under this assumption let's now evaluate the two contributions to the free energy. The potential energy is trivial: $U = mgHN/2$, where N is the number of molecules in the atmosphere and m is their mass. To estimate entropy we figure out that per molecule there is volume $v = AH/N$, where A is Earth surface. The entropy per molecule is then $\ln(n_q v)$ and the entropy of all molecules $S = N \ln(AHn_q/N)$. Then we are minimizing $F = mgHN/2 - k_B T N \ln(AHn_q/N)$ with respect to H .

$$\frac{\partial F}{\partial H} = \frac{mgN}{2} - \frac{k_B T}{H} = 0, \quad (2)$$

which leads to a correct estimation of the atmosphere width of $H = 2k_B T/mg$, which is even kind of precise since the average height of the molecules is $H^* = H/2 = k_B T/mg$ exactly as for the exponential decay.

2. Charge screening in electrolytes and plasmas. Debye-Hückel length

In electrolytes and in plasmas opposite charges tend to be close each other and screen each other electric field. Similarly, the screen the externally introduced electric fields: the positive charges are repelled by, say, a positively charged plate and the negative charges are drawn closer. For sufficiently weak fields the extra charges do not condense onto the

plate (or onto each other) as they are trying to keep some entropy, and stay within some characteristic *screening* length ξ from the plate. The charge distribution in electrolytes in general is described by a nonlinear Poisson-Boltzmann equation that is essentially a Poisson equation for the electric field where the charges are distributed according to the Boltzmann statistics $n \propto \exp(-\phi Ze/k_B T)$, where ϕ is the field potential and Ze is the ion charge. The linearized form of this equation (for weak potentials ϕ) is known as Debye-Hückel approximation and the resulting screening length bears their names.

Let's derive it from simple considerations: let's assume an infinite plate with a charge density σ is immersed into an electrolyte solution of charges $Z_i e$ with concentrations $n_{i,0}$. As in the atmosphere case we will assume a step concentration profile near the plate, with the important difference that the concentrations in the plate vicinity are only slightly different from the concentrations far away. This assumption corresponds to the linear approximation of the Poisson-Boltzmann equation, i.e. to the Debye-Hückel approximation. Thus for each ion type i , we assume:

$$n_i = \begin{cases} n_{i,0} + \Delta n_i, & \text{for } x < \xi \\ n_{i,0}, & \text{for } x > \xi \end{cases} \quad (3)$$

We assume that the charges within the layer ξ totally screen the plate charge: $\sigma = -\sum_i Z_i e \Delta n_i \xi$ and we use the knowledge that the minimization of the free energy will lead the demand that the chemical potentials of each specie are the same in the vicinity of the plate and far away:

$$\Delta \mu_i \approx \frac{2\pi\sigma Z_i e \xi}{4\epsilon} + k_B T \frac{\Delta n_i}{n_{i,0}} = 0 \quad (4)$$

The first term here describes the difference in the chemical potentials of molecules in plate vicinity and far away arising from the electric field: $2\pi\sigma/\epsilon$ is the field strength near the plate, we halve it once to take into account that the field decays to zero at the far end of the layer, so that at that end the potential is $\sim 2\pi\sigma Z_i e \xi / 2\epsilon$ and then halve it once more to "average" the potential over the layer. The second term stems from the change in entropy between the two compartments. We estimate the entropy per molecule the same way as in the atmosphere case: $= \ln n_q/n_i$, the change in the entropy will be a differential of the ln as in the equation above. From there we have:

$$\Delta n_i = -\frac{\pi\sigma Z_i e n_{i,0} \xi}{2k_B T \epsilon} \quad (5)$$

Substituting this now into the equation for neutralization of the plate charge $\sigma = -e\xi \sum_i Z_i e \Delta n_i$ we'll find

$$\xi = \sqrt{\frac{2k_B T \epsilon}{\pi e^2 \sum_i Z_i^2 n_{i,0}}} \quad (6)$$

This is within 20% of the precise result. Notice that both positive and negative charges contribute to screening and that the effect of multivalent ions is much stronger than monovalent as it scales with Z^2 .

B. Plotting The Wavefunction

1. Intro

Our goal in this section is to use the simple problem of a particle in a 1D Cartesian box to be able to plot the wave-function, at different orbitals, of a particle in a central force.

The wave-function of a particle in a 1D box is proportional to $\sin\left(\frac{\pi n_x x}{L}\right)$ where L is the size of the box and n_x is a quantum number which describes the momentum in the x axis. We notice that

$$n_x = 1 + \text{the number of zeros}$$

where the number of zeros is the number of times the wave-function is zero inside the box.

2. A Particle In a Coulomb potential

We first describe the particle with new quantum numbers according to the symmetry of the system, which is spherical. Therefore having n_r as for the radial momentum, l_θ as for the angular momentum of the xy plane, and m as for the angular momentum in the z direction. Just as in the 1D particle in a box these quantum numbers are related to the zeros of the wave-function. In order to be set with the conventional symbols we write,

$$\begin{aligned} l &= l_\theta + |m| \\ n &= n_r + l + 1 \end{aligned}$$

where $-l < m < l$ and l describes the entire angular momentum with eigenvalues $L = \hbar\sqrt{l(l+1)}$, and n describes the energy level. Now we describe the particle with the quantum numbers n, m, l . The wave function is,

$$\psi = R(r)T(\theta)P(\phi)$$

1. Orbital 1S

$n=1, l=0 \rightarrow n_r=0, l_\theta=0, m=0$ This means that we don't have a zero in non of the functions R, T and P, meaning the angular dependence is a constant (T=const, P=const). For the radial dependence we would need to look at the potential energy $U = -\frac{e^2}{r}$,

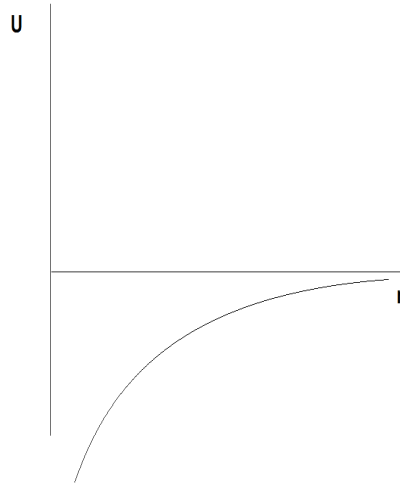


FIG. 1: Coulomb potential

this tells us that particle feels attraction at all distances, and it gets stronger as the particle gets closer to the source, meaning that the probability to find it at the source is the largest and getting smaller as we go to large distances, This means that R looks probably like this,

Now we can plot ψ without having a mathematical representation:

2. Orbital 2S

$n=2, l=0 \rightarrow n_r=1, l_\theta=0, m=0$ This means that we don't have a zero in the functions T and P, and 1 zero in R. From the same considerations we had for 1S, we get

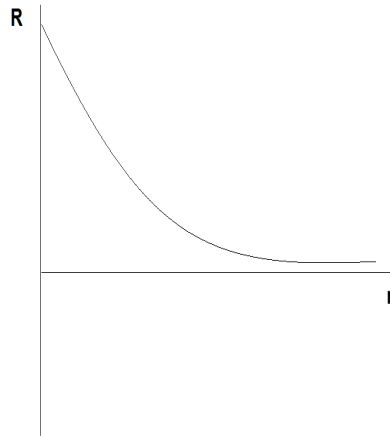


FIG. 2: The radial part of the wave function for the orbital 1S

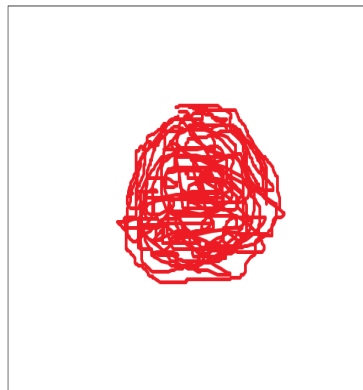


FIG. 3: 1S orbital, a look from above

3. Orbital 2P

$$n=2, l=1 \rightarrow n_r=0$$

Case1: $l_\theta = 1, m=0$

The angular momentum causes the effective potential to change to $U_{eff} = -\frac{e^2}{r} + \frac{L^2}{2Mr^2}$ where M is the reduced mass.

this tells us that particle feels attraction at distances greater than the minimum of U_{eff} and rejection at smaller distances, meaning that the probability to find it at the

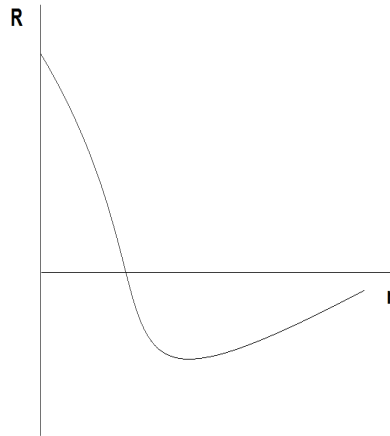


FIG. 4: The radial part of the wave function for the orbital 2S

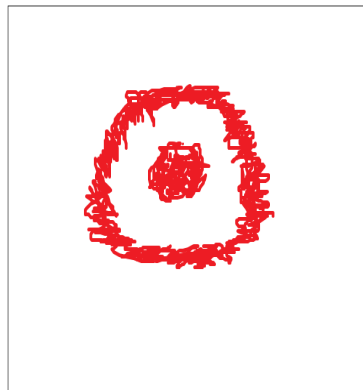


FIG. 5: 2S orbital, a look from above

source goes to zero and the probability to find it far away from the source also goes to zero, because there is attraction, and $n_r = 0$ which means that there is no zero in the R function. This suggests that R probably looks like this,

the P function is constant as $m=0$ and the T function has 1 zero. If we note that the T function get it's biggest absolute values at 0 and π we would get

Now ψ would look something like this,

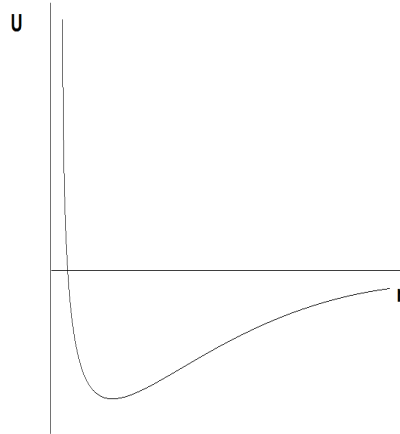


FIG. 6: Coulomb effective potential

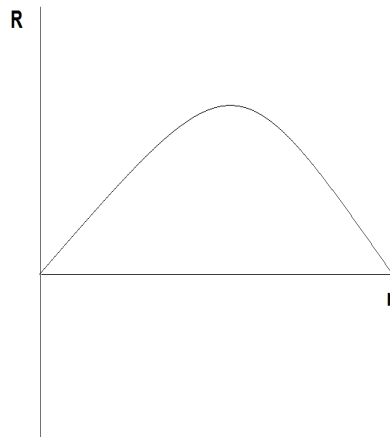


FIG. 7: The radial part of the wave function for the orbital 2P

Case2: $l_\theta = 0, m = \pm 1$

m has two options, \pm , which gets P to have $2|m|$ zeros, meaning for the orbital 2P it has 2 zeros, and so P would probably look something like this,

Because of the rejection l_θ cannot stay constant, therefore T , which has 0 zeros probably look something like this,

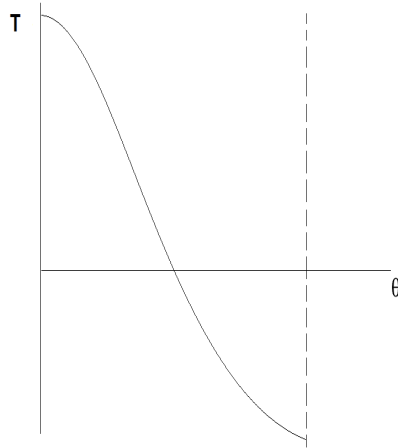


FIG. 8: The polar angle part of the wave function for the orbital 2P for $m=0$

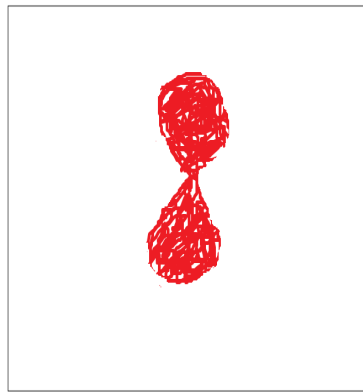


FIG. 9: 2P orbital, a look from the side, for $m=0$

Now ψ would look something like this,

For the rest of the orbitals we continue in this way.

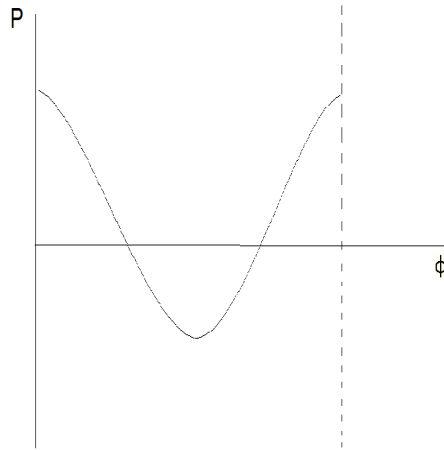


FIG. 10: The azimuth angle part of the wave function for the orbital 2P for $m=\pm 1$

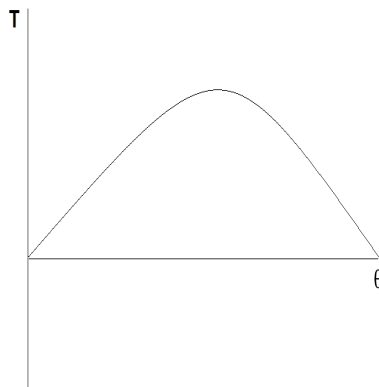


FIG. 11: The polar angle part of the wave function for the orbital 2P for $m=\pm 1$

C. Finding the radius and ionization energy of various atoms

1. The Hydrogen atom

We start the approximation with the hydrogen atom of which we know the radius (Bohr radius) and the ionization energy ($- \text{Rydberg} = 13.6eV$) so we could test our theory. The energy in the system, $E = \langle H \rangle$, is expected to be at the minimum, therefore we will try

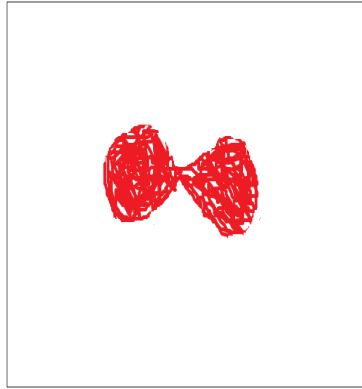


FIG. 12: 2P orbital, a look from the side, for $m=\pm 1$

various of simple wave functions, $\psi\left(\frac{r}{R}\right)$, in the Schroedinger equation.

$$H\psi = -\frac{\hbar}{2m}\nabla^2\psi - \frac{e^2}{r}\psi$$

We then use the variation principle to find E and R (minimize E with regard to R, where R is the atom's radius) and the wave function to give us the minimal energy is the one best describing the wave function of that atom. For hydrogen we find that $\psi = Ce^{-\frac{r}{R}}$ describes perfectly the known data (this is not a surprise since this is the exact solution to the Schroedinger equation). Normalization

$$\int_0^\infty |\psi|^2 4\pi r^2 dr = 1$$

gives $C = \frac{1}{\sqrt{\pi R^3}}$, meaning

$$\psi = \frac{1}{\sqrt{\pi R^3}} e^{-\frac{r}{R}}$$

The kinetic energy is

$$K = \langle E_k \rangle = \int \psi^* \left(-\frac{\hbar}{2m}\nabla^2\right) \psi d^3r = \frac{\hbar^2}{2mR^2}$$

The potential energy is

$$U = \langle E_p \rangle = \int \psi^* \left(-\frac{e^2}{r}\right) \psi d^3r = -\frac{e^2}{R}$$

minimizing $E=K+U$, $\frac{\partial E}{\partial R} = 0$, would give us $R = \frac{\hbar^2}{me^2} = a_B$

and $E_{ionization} = \frac{e^2}{2a_B} = 13.6eV = -R_y$

2. The Helium atom

The helium atom has 2 protons and 2 electrons, the Hamiltonian is

$$H = -\frac{\hbar}{2m} \nabla_1^2 - \frac{e^2}{r_1} - \frac{\hbar}{2m} \nabla_2^2 - \frac{e^2}{r_2} + \frac{e^2}{r_{12}}$$

we would assume that the two electrons has the same wave function as the Hydrogen's, and with the same distance from the source, R (in helium the electrons sit together at the 1S orbital, therefore the same radius).

$$\psi_1 \sim e^{-\frac{r_1}{R}}, \psi_2 \sim e^{-\frac{r_2}{R}}$$

So just as for the hydrogen atom, remembering that now the charge of the nuclei is twice than that in the hydrogen atom, we would get

$$E = \langle H \rangle = \frac{\hbar^2}{2mR^2} + \frac{\hbar^2}{2mR^2} - \frac{Ze^2}{R} - \frac{Ze^2}{R} + \beta \frac{e^2}{R}$$

where we educatedly guessed the last part because of the resemblance to the hydrogen potential energy, β is a number still to be found, and $Z=2$ is the number of protons in the nuclei. The direct way to find β is

$$\langle \frac{e^2}{r_{12}} \rangle = \int |\psi(\vec{r}_1)|^2 |\psi(\vec{r}_2)|^2 \frac{1}{r_1 - r_2} d\vec{r}_1 d\vec{r}_2$$

we would look for a shorter way to solve this problem:

we would use the symmetry of the problem and find this potential energy as in a simple charge distribution problem, where now ψ would be the charge density. Contrary to this simple problem in our problem we would need to sum over the contributions twice, because now we want to add all the possibilities and we have 2 wave functions. Therefore we would get,

$$\begin{aligned} U_{12} &= 2 \sum q(r) \phi = 2 \int_0^\infty \frac{q(r)}{r} |\psi|^2 4\pi r^2 dr \\ q(r) &= \int_0^\infty |\psi|^2 4\pi r'^2 dr' \\ \psi &= \frac{1}{\sqrt{\pi R^3}} e^{-\frac{r}{R}} \end{aligned}$$

$$\text{this gives } U_{12} = \frac{5}{8} \frac{e^2}{R} \rightarrow \beta = \frac{5}{8}.$$

The energy is now

$$E = \frac{2\hbar^2}{2mR^2} - (4 - \beta) \frac{e^2}{R}$$

β is rising the system's energy, therefore we would expect R to be bigger than if there was only one electron in the system ($\beta = 0$). Minimization of E gives $E_{ionization} = 5.7R_y$, and $R = 0.59a_B$ for the 2 electrons case. For the one electron case we get $E_{ionization} = 4R_y$, and $R = 0.5a_B$. This tells us that the energy needed to ionize the helium atom from the first electron takes $1.7R_y$ and from the second one it is $4R_y$. We can think of it as though the first electron is shielding the second electron from the nuclei, If it was completely shielded than the second electron would have felt as though it is a hydrogen atom, $E_{ionization} = R_y$. The real result from the experimental data, for the unionizes case, is $E = -5.8R_y$. Our result

is amazingly close to the real one considering all the assumptions we made. This means that the real wave function is close to the one we chose (the exponent).

3. The general case

The result of the helium case taught us of the shielding effect. For Li which has 3 electrons, the 3rd electron is in the 2S orbital which is at greater radius than 1S, therefore the electrons of the lower radius are shielding the 3rd electron from the nuclei and it is as though there is only 1 proton in the nuclei, $Z_{eff} = Z - k$ where k is the number of electrons in all the lower energy levels, For example for the second row in the table of contents k=2 and for the 3rd k=10.

The energy ,after choosing the same exponent wave function, is

$$E = \frac{\hbar^2 n^2 N}{2mR^2} - \frac{NZ_{eff}e^2}{R} + \frac{N(N-1)\beta e^2}{2R}$$

where N is the number of electrons in the outer orbitals, $\beta = \frac{5}{8}$, and n is the energy level. After minimizing E we get that R is

$$R = \frac{2n^2 a_B}{2Z_{eff} - (N-1)\beta}$$

The energy is

$$\frac{E(Z_{eff}, N)}{R_y} = \frac{N}{4n^2} [2Z_{eff} - (N-1)\beta]^2$$

From these results of the binding (or ionizing) energies we can understand some of the effects of atoms binding to create a molecule or a lattice , why the distance between 2 atoms in a molecule is about 3\AA and etc.

4. Estimating the Young modulus

As we saw in the previous lectures $E \sim 10^{10} P_a \left[\frac{N}{n^3} \right] = \left[\frac{J}{m^3} \right]$. Because of the units we would expect the Young modulus to be of the order of

$$\frac{e^2}{4\pi\epsilon_0 d^4} = \frac{(1.6 \cdot 10^{-19})^2}{10 \cdot 10^{-11} \cdot (3 \cdot 10^{-10})^4} \approx 3 \cdot 10^{10}$$

This is the order of magnitude that the experiments give for the Young modulus of the various materials. Now we understand the reason for that.