Notes on the Variational Method

1 Overview and Simple Examples: after Griffiths

Last semester we found the ground state energy and wave function by solving (exactly or numerically) a Schroedinger equation. It is both conceptually and practically useful to consider the following, slightly different, point of view:

Finding the exact ground state of a system is equivalent to minimizing the expectation value of the Hamiltonian in the space of normalized wave functions obeying the relevant boundary conditions. Finding an approximate ground state is equivalent to minimizing the Hamiltonian in a restricted subspace of wave functions.

The proof is simple and is given in any textbook: for a given Hamiltonian $H$ and normalized wave function $\psi$ consider the expectation value

$$E = \langle \psi | H | \psi \rangle = E_0 = \langle \phi | H | \phi \rangle$$  \hspace{1cm} (1)

To prove Eq 1 expand $\psi$ in the basis of exact eigenstates $\phi_n$:

$$\psi = \sum_{n=0,\infty} a_n \phi_n$$  \hspace{1cm} (2)

with (normalization)

$$\sum_{n=0,\infty} |a_n|^2 = 1$$  \hspace{1cm} (3)

Because the $\phi_n$ are eigenstates of $H$ the left hand side of Eq 1 becomes

$$\sum_{n,0,\infty} E_n |a_n|^2 = E_0 |a_0|^2 + \sum_{n=1,\infty} E_n |a_n|^2$$  \hspace{1cm} (4)

$$= E_0 (1 - \sum_{n=1,\infty} |a_n|^2) + \sum_{n=1,\infty} E_n |a_n|^2$$  \hspace{1cm} (5)

$$= E_0 + \sum_{n,1,\infty} (E_n - E_0) |a_n|^2 \geq E_0$$  \hspace{1cm} (6)

where in the second line we used the normalization of the wave function and in the third line we obtained a bound because the ground state energy is by definition the lowest energy. Evidently the bound is only saturated if $a_n = 0 \forall n \neq 0$, in other words if $\psi = \phi_0$.

Suppose that the wave function $\psi$ is 'close' to the ground state wave function $\phi_0$. 'Close' means that the coefficients $a_{n>0}$ are small and that $|a_0|$ is near unity.
so that $\sum_{n>0} |a_n|^2$ is small). We see that deviations of $E$ from $E_0$ are quadratic in the $a_{n>0}$. Thus even a poor approximation to the wave function may yield a decent estimate for the energy and conversely accuracy of energy is no guarantee of accuracy of wave function.

Eq 1 suggests a strategy for estimating the ground state energy of a system: guess a wave function with some adjustable parameters, and adjust them until the energy is minimized. Eq 1 guarantees that the energy you obtain is greater than the ground state energy; Eq 6 suggests that your estimate will be quite reasonable.

2 Formalization of Variational Argument: Lagrange Multipliers

The expectation value in Eq 1 is a member of the class of mathematical objects known as 'functionals'. Just as a simple function of one variable is a machine which 'eats' a number and spits out a number, a functional is a machine which eats a function and spits out a number. In our example the value of $E$ depends on the entire function $\psi$. Minimization is a standard problem in the theory of functionals; it is often referred to as 'the calculus of variations'. For essentially the reasons encountered last semester in defining Hilbert spaces, formulating the subject in a manner which satisfies a mathematician is difficult—but actually working with the kinds of functionals which appear in quantum mechanics is relatively simple.

Consider, therefore, the problem of minimizing the functional

$$E[\{\psi^*, \psi\}] = \int dx \psi^*(x) \hat{H} \psi(x)$$

(7)

over the space of normalized wave functions $\psi$ which depend on some coordinates $x$. Here $\hat{H}$ is a Hermitian operator (in what follows we will take it to be the Hamiltonian of a system).

Note that we must minimize in not with respect to all functions, but rather with respect to the subset of functions which obey a constraint, namely that $\int dx |\psi(x)|^2 = 1$. To deal with minimization of a constrained system, it is very convenient to use the method of Lagrange multipliers: consider a new object $E'$ which is a functional of $\psi$ and a function of a new parameter $\lambda$:

$$E'[\{\psi^*, \psi\}, \lambda] = \int dx \psi^*(x) \hat{H} \psi(x) - \lambda \left( \int dx \psi^* \psi(x) - 1 \right)$$

(8)

If we minimize $E'$ with respect to all possible functions $\psi$ and simultaneously demand that $\partial E'/\partial \lambda = 0$ then we will have obtained the correct extremum. Indeed, explicitly,

$$\frac{\partial E'}{\partial \lambda} = 1 - \int dx \psi^* \psi(x) = 0$$

(9)
guaranteeing normalization. Thus at the price of introducing one more variable we are able to perform an unconstrained minimization.

Denote the function which minimizes $E'$ by $\phi_0$, and consider a $\psi(x) = \phi_0(x) + \delta \psi(x)$. We saw in the previous section that the change in $E'$ is quadratic in small deviations of the wave function about the optimum one. This means that the terms in $E$ which are linear in $\delta \psi(x)$ or its complex conjugate $\delta \psi^*(x)$ (which we denote $\delta E/\delta \psi(x)$ or $\delta E/\delta \psi^*(x)$ respectively) must vanish.

Let us compute the effect on $E'$ of making a small change, $\delta \psi^*$, in $\psi^*$:

$$E'[\{\phi_0^* + \delta \psi^*, \phi_0\}, \lambda] = E'[\{\phi_0^*, \phi_0\}, \lambda] + \int dx \delta \psi^*(x) \hat{H} \phi_0(x) - \lambda \int dx \delta \psi^*(x) \phi_0(x) + O(\delta \psi^2)$$

At the extremum, the linear term must vanish for any $\delta \psi^*(x)$, implying that $\phi_0$ must satisfy

$$\hat{H} \phi_0(x) = \lambda \phi_0(x) \quad (11)$$

Eq 11 is the familiar Schrödinger equation and we see that in this case if $\lambda$ is an eigenvalue and $\phi_0$ is the associated eigenfunction we have an extremum. Evaluating $E'$ using one of these solutions yields

$$E' = \lambda; \quad (12)$$

the minimum is obviously obtained when $\lambda$ is the ground state energy.

3 Hartree and Hartree-Fock approximation

The development leading to Eq 10 is more than just a fancy way of recovering something you already know. It also applies to minimizing an expectation value over a restricted subspace of wave functions—provided one can easily specify the restriction—and yields Schrödinger-like equations for the minimum energy within that restricted subspace.

Consider the $^2$He problem discussed before. Here we have a Hamiltonian which depends on two particle coordinates $r_1$ and $r_2$:

$$H_{^2He} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|r_1 - r_2|} \quad (13)$$

and an exact wave function which is some function $\psi(r_1, r_2) \chi_S(\sigma_1, \sigma_2)$ of both coordinates and also of both spins. The ground state wave function is a spin singlet, and so is even under interchange of the particle coordinates. If the electron-electron interaction term were negligible, the space part of the ground state wave function would be the product of two 1S wave functions $\psi(r_1, r_2) = \phi_{1S}(r_1)\phi_{1S}(r_2)$.

Let us now seek the lowest energy singlet state where the space part of the wave function takes the same product form.
\[
\psi_{\text{approx}}(r_1, r_2) = \psi_1(r_1)\psi_2(r_2) \tag{14}
\]

with normalized functions \(\psi_{1,2}(r)\) (which will turn out to be the same) to be determined. We will assume that both are spherically symmetric and that the ground state is a spin singlet (so the wave function is even under interchange of coordinates). Because we have two functions to be normalized, we will need two Lagrange multipliers, so we must minimize:

\[
E'' = \langle \psi_{\text{approx}} | H_{He} | \psi_{\text{approx}} \rangle - \lambda_1 \left( \int d^3r_1 |\psi_1(r_1)|^2 - 1 \right) - \lambda_2 \left( \int d^3r_2 |\psi_2(r_2)|^2 - 1 \right) \tag{15}
\]

Varying this equation with respect to \(\psi_{1,2}(r)\) and using the normalization equations which follow from the variation with respect to \(\lambda_{1,2}\) gives

\[
\lambda_1 \psi_1(r_1) = -\frac{\hbar^2}{2m} \nabla^2 \psi_1(r_1) - \frac{2e^2}{r_1} \psi_1(r_1) + \left( \int d^3r_2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} |\psi_2(r_2)|^2 \right) \psi_1(r_1) \tag{16}
\]

\[
\lambda_2 \psi_2(r_2) = -\frac{\hbar^2}{2m} \nabla^2 \psi_2(r_2) - \frac{2e^2}{r_2} \psi_2(r_2) + \left( \int d^3r_2 \frac{e^2}{|\vec{r}_2 - \vec{r}_1|} |\psi_1(r_1)|^2 \right) \psi_2(r_2) \tag{17}
\]

The equations for \(\psi_{1,2}\) are seen to be identical, and are seen to be Schrödinger equations involving a potential

\[
V_{\text{eff}}(r) = -\frac{2e^2}{r} + \int d^3r_2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} |\psi_2(r_2)|^2 \tag{18}
\]

which has two terms: the Coulomb potential from the nuclear charge and the Coulomb potential from the other electron. Thus in this approximation each electron moves in the average potential created by the charge density of the other electron, and this charge density must be computed self consistently from the solution to the equations.

The variational solution given in Griffiths amounts to finding an approximate solution of Eq 15.

The procedure outlined above is called the Hartree-Fock approximation, after the two physicists who introduced it. In general it yields a set of \(N\) coupled nonlinear equations (one for each particle), involving effective potentials which are generally more complicated than just the 'screened coulomb' form found above. In the problem set I ask you to derive the equations in the simplest nontrivial case.