

Lecture 18, March 15, 2014 (correcting an error in 2006 notes)

Solved Homework

If the approximate energy is given by

$$\langle H \rangle = 3a^4 - 4a^3 - 36a^2 + 10$$

where a is a variational parameter, local minima and maxima of the energy will correspond to stationary points of $\langle H \rangle$ with respect to a , i.e., points where

$$\frac{d\langle H \rangle}{da} = 0$$

Setting the derivative equal to zero gives

$$0 = 12a^3 - 12a^2 - 72a$$

which may be simplified as

$$0 = a(a^2 - a - 6) = a(a - 3)(a + 2)$$

The three solutions to this cubic equation are $a = -2$, 0 , and 3 . It is a trivial matter to plug these values back into the expression for the energy and find that the corresponding values of $\langle H \rangle = E$ are -54 , 10 , and -219 . Analysis of the sign of the second derivative of $\langle H \rangle$ with respect to a indicates these values to be a local minimum, a local maximum, and a local minimum, respectively (although their characters are obvious in this case).

The variational principle states that our lowest energy (-219) will be an upper bound to the true lowest energy (which would be the ground-state energy), so the highest energy the system can possibly have in its ground state is -219 (in whatever units a is expressed).

Some Simple Variational Calculations

Last lecture, we considered the variational principle in the context of basis functions and their uses for molecular calculations. The variational approach provides a prescription for computing molecular orbitals as linear combinations of atomic orbitals,

where the coefficients of the linear combinations are the variational parameters subject to optimization. However, to better appreciate some of the concepts associated with the variational principle, let's now take a step back and focus on a vastly simpler system with only a single variational parameter.

Consider the ground state for a particle having mass 1 a.u. in a box of length $L = 1$ a.u. We know the eigenfunction and eigenvalue (in a.u.) for this particle-in-a-box system exactly, namely

$$\begin{aligned}\Psi_1(x) &= \sqrt{2} \sin(\pi x) \quad 0 \leq x \leq 1 \\ E_1 &= \frac{\pi^2}{2}\end{aligned}\tag{18-1}$$

Now, let us imagine that we had no idea how to derive the correct eigenfunction. But, we certainly imagine that the function should have no nodes (it's the ground state, after all), and we also know from the boundary conditions it must be zero at both ends of the box. One very simple choice for a trial function might be

$$\xi(x) = x(1-x)\tag{18-2}$$

This function has the correct behavior at $x = 0$ and $x = 1$ and it is everywhere positive in between. Of course, there's no variational parameter in ξ , so there is nothing there to optimize. A simple way to introduce such a parameter is to choose instead

$$\xi(x;a) = x^a(1-x)\tag{18-3}$$

where a is the variational parameter to be optimized. The optimization condition minimizes the energy of the trial wave function, which from the variational principle establishes an upper bound on the "true" energy. The variational condition is

$$0 = \frac{d}{da} \left[\frac{\langle \xi(x;a) | H | \xi(x;a) \rangle}{\langle \xi(x;a) | \xi(x;a) \rangle} \right]\tag{18-4}$$

Recall that for the particle in a box, $H = T$ (there is no potential energy component of the Hamiltonian), so we have three steps in the optimization of a . Step 1 is to evaluate the integral in the numerator of eq. 18-4, step 2 is to evaluate the square modulus of ξ in the denominator of eq. 18-4, and step 3 is to take the derivative of the ratio and determine the value of a that causes that derivative to be zero (and thereby minimizes the energy).

So, let's start with step 2, determining the square modulus of ξ . We have

$$\begin{aligned}
\langle \xi(x;a) | \xi(x;a) \rangle &= \int_0^1 x^a (1-x) x^a (1-x) dx \\
&= \int_0^1 x^{2a} dx - 2 \int_0^1 x^{2a+1} dx + \int_0^1 x^{2a+2} dx \\
&= \frac{x^{2a+1}}{2a+1} \Big|_0^1 - 2 \frac{x^{2a+2}}{2a+2} \Big|_0^1 + \frac{x^{2a+3}}{2a+3} \Big|_0^1 \\
&= \frac{1}{2a+1} - \frac{2}{2a+2} + \frac{1}{2a+3} \\
&= \frac{2}{(2a+1)(2a+2)(2a+3)}
\end{aligned} \tag{18-5}$$

Now, we will consider the expectation value of H , which is

$$\langle \xi(x;a) | H | \xi(x;a) \rangle = \int_0^1 x^a (1-x) \left(-\frac{1}{2} \frac{d^2}{dx^2} \right) [x^a (1-x)] dx \tag{18-6}$$

The second derivative of ξ with respect to x is

$$\begin{aligned}
\frac{d^2}{dx^2} [x^a (1-x)] &= \frac{d}{dx} \left\{ \frac{d}{dx} [x^a (1-x)] \right\} \\
&= \frac{d}{dx} [ax^{a-1} (1-x) - x^a] \\
&= a(a-1)x^{a-2} (1-x) - ax^{a-1} - ax^{a-1} \\
&= (a^2 - a)x^{a-2} - (a^2 + a)x^{a-1}
\end{aligned} \tag{18-7}$$

Inserting this result into eq. 18-6 gives

$$\begin{aligned}
\langle \xi(x;a) | H | \xi(x;a) \rangle &= -\frac{a}{2} \left[\int_0^1 (a-1)x^{2a-2} dx - \int_0^1 2ax^{2a-1} dx + \int_0^1 (a+1)x^{2a} dx \right] \\
&= -\frac{a}{2} \left(\frac{a-1}{2a-1} - 1 + \frac{a+1}{2a+1} \right) \\
&= \frac{a}{2(2a-1)(2a+1)}
\end{aligned} \tag{18-8}$$

So, we now have

$$\begin{aligned} \frac{\langle \xi(x;a)|H|\xi(x;a) \rangle}{\langle \xi(x;a)|\xi(x;a) \rangle} &= \frac{\frac{a}{2(2a-1)(2a+1)}}{\frac{2}{(2a+1)(2a+2)(2a+3)}} \\ &= \frac{2a^3 + 5a^2 + 3a}{4a - 2} \end{aligned} \quad (18-9)$$

We want the derivative of this expression with respect to a to be zero, so we have

$$\begin{aligned} 0 &= \frac{d}{da} \left(\frac{2a^3 + 5a^2 + 3a}{4a - 2} \right) \\ &= \frac{(6a^2 + 10a + 3)(4a - 2) - 4(2a^3 + 5a^2 + 3a)}{(4a - 2)^2} \\ &= \frac{16a^3 + 8a^2 - 20a - 6}{16a^2 - 16a + 4} \end{aligned} \quad (18-10)$$

Thus, we need to find values of a that make the numerator of eq. 18-10 zero (and check to be sure that they do not make the denominator simultaneously zero, since that result would be undefined). While there is no completely general way to solve the cubic equation in the numerator, trial and error gives $a = 1.043$ to better than 1% accuracy.

Thus, within the limits of our functional form, the best ξ is

$$\xi(x; a_{\text{opt}}) = x^{1.043} (1 - x) \quad (18-11)$$

We can use this value of a in eq. 18-9 to arrive at

$$\begin{aligned} \frac{\langle \xi(x;a)|H|\xi(x;a) \rangle}{\langle \xi(x;a)|\xi(x;a) \rangle} &= \frac{\frac{1.043}{2(2.086-1)(2.086+1)}}{\frac{2}{(2.086+1)(2.086+2)(2.086+3)}} \\ &= 4.99 \end{aligned} \quad (18-12)$$

So, the upper bound on the ground state energy is 4.99 a.u. How does this compare with the exact result? If we reduce E from eq. 18-1 to a decimal, it is 4.93 a.u. Our error with this functional form for ξ is 0.06 a.u., or just a bit more than 1%!

How does ξ do for a different property? Consider $\langle x \rangle$ evaluated for ξ . That is

$$\begin{aligned}
\langle \xi(x;a)|x|\xi(x;a) \rangle &= N^2 \int_0^1 x^a (1-x)(x) [x^a (1-x)] dx \\
&= 32.066 \left(\int_0^1 x^{2a+1} dx - 2 \int_0^1 x^{2a+2} dx + \int_0^1 x^{2a+3} dx \right) \\
&= 32.066 \left(\frac{1}{2a+2} - \frac{2}{2a+3} + \frac{1}{2a+4} \right) \quad (18-13) \\
&= 32.066 \left(\frac{1}{2.086+2} - \frac{2}{2.086+3} + \frac{1}{2.086+4} \right) \\
&= 0.507
\end{aligned}$$

where N is the normalization constant for ξ (the square root of one over the square modulus computed in eq. 18-5). Note that the exact answer for the particle in a box is 0.5 for $\langle x \rangle$ —the middle of the box. So, our wave function ξ is a bit skewed to the right, and our error is about 1%.

We might have considered an alternative trial wave function, namely

$$\xi(x;a) = x^a (1 - x^2) \quad (18-14)$$

By following a procedure identical to the one above (but with the math not shown), one arrives at an optimal value for a of 0.862, and with this value one computes $\langle H \rangle = 5.15$. This energy is in error by 0.22 a.u., i.e., it has *increased* the error compared to eq. 18-11 by almost a factor of 4. For $\langle x \rangle$, the prediction using the form for ξ of eq. 18-14 is 0.52. So, this newer trial function skews a bit further to the right of the center of the box, but the additional error is not as large. This is a fairly typical situation: just because you affect the trial function for purposes of computing the energy does *not* necessarily imply that you will see similar changes in other expectation values. It is a *reasonable* assumption that one expectation value will improve or degrade similarly to the energy, but it is not *guaranteed*. Plots of the two approximate wave functions and the exact wave function are provided below, and illustrate the skewness that shows up in $\langle x \rangle$. The closeness of both approximate wave functions to the exact one is apparent, however.

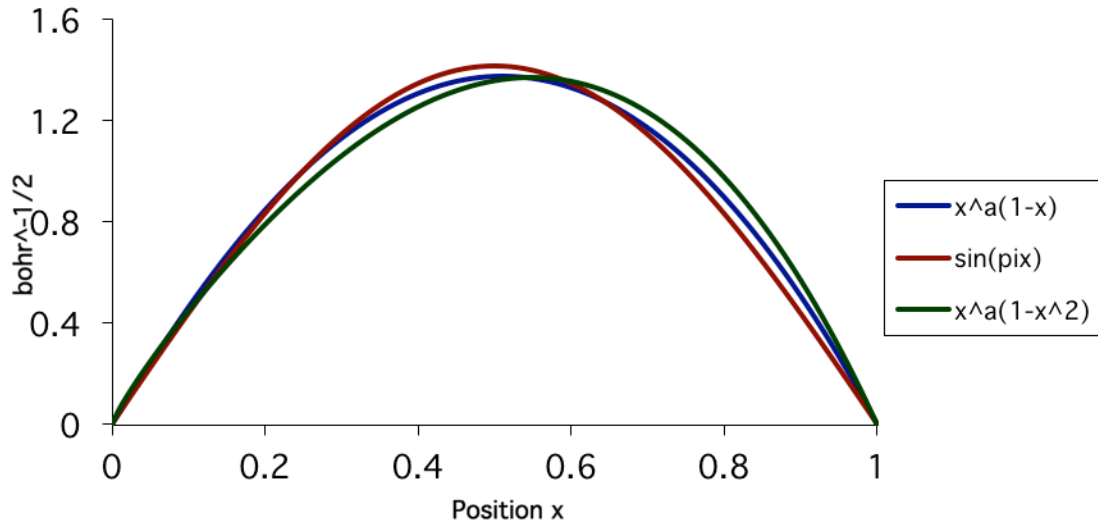
To wrap this up, given our results so far, it seems as though one obvious thing to do might be to define a new trial function according to

$$\xi(x;a,b) = x^a (1 - x^b) \quad (18-15)$$

where b seems likely to be less than one. With this trial function, the variational condition would require

$$0 = \frac{d}{da} \left[\frac{\langle \xi(x;a,b)|H|\xi(x;a,b) \rangle}{\langle \xi(x;a,b)|\xi(x;a,b) \rangle} \right] \quad \text{and} \quad 0 = \frac{d}{db} \left[\frac{\langle \xi(x;a,b)|H|\xi(x;a,b) \rangle}{\langle \xi(x;a,b)|\xi(x;a,b) \rangle} \right] \quad (18-16)$$

Particle in a Box Ground States



Following a protocol just like that above, we could generate these two equations in two unknowns and solve for a and b . The exercise is left for the interested student... To make connection with the previous lecture, however, note that each new parameter in the trial function introduces a new derivative equation, so that one inevitably ends up with N equations in N unknowns where the number of parameters is N . The secular equation is simply the use of linear algebra to solve these equations for the LCAO approach.

The Helium Atom

Helium has a nucleus with two protons and two electrons. The proper non-relativistic electronic Hamiltonian in a.u. is thus

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \quad (18-17)$$

where the terms on the r.h.s. correspond to, in order, the kinetic energy of electron 1, the kinetic energy of electron 2, the attraction of electron 1 to the nucleus (r_1 is the distance between the nucleus and electron 1), the attraction of the electron 2 to the nucleus (r_2 is the distance between the nucleus and electron 2), and the repulsion between electron 1 and electron 2 (r_{12} is the distance between the two electrons). Alas, the Schrödinger equation involving the Hamiltonian of eq. 18-17 has no analytic solutions. So, perforce we are left to try and come up with trial wave functions!

One seemingly reasonable wave function might be to assume that, as a first approximation, we can ignore the interelectronic repulsion term (the last term on the r.h.s. of eq. 18-17). If we do that, the remaining Hamiltonian is simply the sum of the usual

one-electron Hamiltonian for electron 1 and for electron 2. That is, an exact wave function would be

$$\Psi(1,2) = \psi(1)\psi(2) \quad (18-18)$$

where ψ is a usual one-electron hydrogenic orbital. For the ground state of He, we'd assume each ψ was a 1s orbital. If we then evaluate $\langle \Psi | H | \Psi \rangle$ for the *correct* Hamiltonian of eq. 18-17 using the *approximate* wave function of eq. 18-18 (lots of extraordinarily tedious calculus—not shown) we obtain an energy of -2.75 a.u. The exact answer (determined through heroic variational calculations, since the solution cannot be obtained analytically) is -2.90 a.u. (experiment gives the same value, of course). So, the error is 0.15 a.u. If that number seems small, we should perhaps convert to a more intuitive set of units. That is an error of $94.1 \text{ kcal mol}^{-1}$ in the total electronic energy—rather a lot.

One way to improve this calculation is to maintain the functional form of eq. 18-18, but instead of the usual s orbital wave function that has the nuclear charge in the exponential, i.e.,

$$\psi_{100}(r, \theta, \phi) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr} \quad (18-19)$$

we treat the nuclear charge *itself* as a variational parameter. The physical reason for such an approach is that we may think of the second electron as “getting in the way” of the first electron seeing the full nuclear charge. Thus, we take as our one-electron wave function

$$\psi_{100}(r, \theta, \phi) = \frac{\eta^{3/2}}{\sqrt{\pi}} e^{-\eta r} \quad (18-20)$$

where η is the variational parameter. Minimization of the energy with respect to this parameter gives $\eta = 1.69$ (reduced from 2, in keeping with our physical picture of why it varies) and an energy of -2.85 a.u. Thus, the error has been reduced by 67%!

With still more complicated functional forms and/or more flexibility in variational parameters, one can do still better. In the 1950s, He was pretty much solved, with energies accurate to $0.000\ 000\ 001$ a.u. being obtained from variational expressions involving more than 1000 variational parameters. The wave functions themselves are not very intuitive, but they can, of course, be used in the evaluation of expectation values for other operators.

Homework

To be solved in class:

Evaluate $\langle p_x \rangle$ for the ξ of eq. 18-11. What does the result mean? (Don't forget to normalize ξ .)

To be turned in for possible grading Mar. 11:

On the interval 0 to 1, what is the square modulus (in terms of a and b) of the trial wave function in eq. 18-15?