Physical Chemistry II (Quantum Mechanics)
Spring Semester 2005
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Solved Homework

We seek

$$\langle \xi(x;a)|p_x|\xi(x;a)\rangle = N^2 \int_0^1 x^a(1-x)\left(-i\hbar\frac{d}{dx}\right)\left[x^a(1-x)\right]dx$$

where N is the normalization constant on ξ. We could do this the usual way (take the derivative, solve all the integrals), but just for fun, let's do something more general.

Consider *any* real wave function of one dimension f.

$$\langle f(x)|p_x|f(x)\rangle = \int_a^b f(x)\left(-i\hbar\frac{d}{dx}\right)f(x)dx$$

$$= -i\hbar\int_a^b f(x)\left(\frac{df(x)}{dx}\right)dx$$

where we have assumed without loss of generality that f is normalized over the integration interval. We can solve the integral using integration by parts. If we use

$$\int_a^b u\,dv = uv\Big|_a^b - \int_a^b v\,du$$

$$u = f(x) \quad dv = \frac{df(x)}{dx}dx$$

$$du = \frac{df(x)}{dx}dx \quad v = f(x)$$

then we may write

$$\int_a^b f(x)\left(\frac{df(x)}{dx}\right)dx = \left[f(x)\right]^2\Big|_a^b - \int_a^b f(x)\left(\frac{df(x)}{dx}\right)dx$$

or

$$\int_a^b f(x)\left(\frac{df(x)}{dx}\right)dx = \frac{1}{2}\left[f(x)\right]^2\Big|_a^b$$

but, we know that a well-behaved wave function must go to zero at its integration endpoints, so the r.h.s. of the final equation is just 0. Thus, *any real wave function* has an expectation value of 0 for the momentum operator. We can think of this result as deriving from a superposition of left- and right-moving particle wave functions.

If you think about this more deeply, it should now be clear why only the the $m_l = 0$ wave functions of the spherical harmonics can be real: they have no z component angular momentum. Those with positive or negative values of m_l are necessarily complex, so we can think of them as rotating, in some sense, either clockwise or counterclockwise, about appropriate axes. When we make linear combinations to get real wavefunctions, the expectation value of L_z necessarily becomes zero—because the wave functions are real—and the linear combinations are no longer eigenfunctions of L_z.

Variational Calculations on the H Atom

As we did with the particle in a box, it is often helpful to consider a system where the answer is known exactly in order to evaluate the utility of different variational protocols. Let us now consider the hydrogen atom. The question in which we are interested is, what if we were to replace the exact 1s wave function

$$\psi_{100}(r,\theta,\phi) = \frac{Z^{3/2}}{\sqrt{\pi}}e^{-Zr} \tag{19-1}$$

with a different functional dependence on r, namely

$$\psi_{1s}(r,\theta,\phi;\alpha) = Ne^{-\alpha r^2} \tag{19-2}$$

where N is the normalization constant and α is a variational constant. We can find N quickly from

$$\langle \psi_{1s}(r,\theta,\phi;\alpha) | \psi_{1s}(r,\theta,\phi;\alpha) \rangle = 1$$

$$= N^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-2\alpha r^2} r^2 dr \sin\theta d\theta d\phi$$

$$= 4\pi N^2 \int_0^\infty r^2 e^{-2\alpha r^2} dr \tag{19-3}$$

$$= 4\pi N^2 \left[\frac{1}{8\alpha} \left(\frac{\pi}{2\alpha} \right)^{1/2} \right]$$

The normalization constant is thus

$$N = \left(\frac{2\alpha}{\pi} \right)^{3/4} \tag{19-4}$$

Our variational condition, given a normalized wave function is

$$0 = \frac{d}{d\alpha}\Big[\big\langle \psi_{1s}(r,\theta,\phi;\alpha)|H|\psi_{1s}(r,\theta,\phi;\alpha)\big\rangle\Big]$$

$$= \frac{d}{d\alpha}\Big[\Big\langle \psi_{1s}(r,\theta,\phi;\alpha)\Big|-\frac{1}{2}\nabla^2 - \frac{1}{r}\Big|\psi_{1s}(r,\theta,\phi;\alpha)\Big\rangle\Big] \qquad (19\text{-}5)$$

so we need to evaluate the expectation values of the kinetic and potential energy operators.

So, let's start with the kinetic energy operator. Recall that in spherical polar coordinates (and a.u.) we have

$$\nabla^2(r,\theta,\phi) = -\frac{1}{r^2}\Big(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - L^2\Big) \qquad (19\text{-}6)$$

In this case, since the angular momentum of an s wave function is 0, we need only consider the r component. So, we have

$$\Big\langle \psi_{1s}(r,\theta,\phi;\alpha)\Big|-\frac{1}{2}\nabla^2\Big|\psi_{1s}(r,\theta,\phi;\alpha)\Big\rangle$$

$$= -\frac{1}{2}\Big(\frac{2\alpha}{\pi}\Big)^{3/2}(4\pi)\int_0^\infty e^{-\alpha r^2}\Big(\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\Big)e^{-\alpha r^2}r^2 dr \qquad (19\text{-}7)$$

where the second line reflects having taken the constants out front, and having integrated over θ and ϕ to get 4π. The remaining integral requires some care to evaluate. Remember that the d/dr operators only operate on the wave function, not on the trailing r^2 that is simply part of the spherical integral volume element. So, first we must differentiate the exponential function once, then multiply by r^2, then differentiate the product once again, then divide by r^2, then finally the volume element can be included and we end up with

$$-\frac{1}{2}\Big(\frac{2\alpha}{\pi}\Big)^{3/2}(4\pi)\int_0^\infty e^{-\alpha r^2}\Big(\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\Big)e^{-\alpha r^2}r^2 dr$$

$$= \Big(\frac{2\alpha}{\pi}\Big)^{3/2}(2\pi)\Big(6\alpha\int_0^\infty r^2 e^{-2\alpha r^2}dr - 4\alpha^2\int_0^\infty r^4 e^{-2\alpha r^2}dr\Big) \qquad (19\text{-}8)$$

To simplify this, we may look in an integral table to find

$$\int_0^\infty r^{2n}e^{-ar^2}dr = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\Big(\frac{\pi}{a}\Big)^{1/2} \qquad (19\text{-}9)$$

So, we have

$$\left(\frac{2\alpha}{\pi}\right)^{3/2}(2\pi)\left(6\alpha\int_0^\infty r^2 e^{-2\alpha r^2}\,dr - 4\alpha^2\int_0^\infty r^4 e^{-2\alpha r^2}\,dr\right)$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/2}(2\pi)\left[6\alpha\left(\frac{1}{4\cdot 2\alpha}\right)\left(\frac{\pi}{2\alpha}\right)^{1/2} - 4\alpha^2\left(\frac{3}{8\cdot 4\alpha^2}\right)\left(\frac{\pi}{2\alpha}\right)^{1/2}\right]$$

$$= \frac{3\alpha}{2} \tag{19-10}$$

Remarkable how sweetly that simplified in the end, isn't it?

Now we need to evaluate

$$\left\langle\psi_{1s}(r,\theta,\phi;\alpha)\left|-\frac{1}{r}\right|\psi_{1s}(r,\theta,\phi;\alpha)\right\rangle$$

$$= -\left(\frac{2\alpha}{\pi}\right)^{3/2}(4\pi)\int_0^\infty e^{-\alpha r^2}\left(\frac{1}{r}\right)e^{-\alpha r^2}r^2\,dr$$

$$= -\left(\frac{2\alpha}{\pi}\right)^{3/2}(4\pi)\int_0^\infty re^{-2\alpha r^2}\,dr \tag{19-11}$$

where again the normalization factor and the 4π from the angular integrals have been brought out front. An integral table gives

$$\int_0^\infty r^{2n+1}e^{-ar^2}\,dr = \frac{n!}{2a^{n+1}} \tag{19-12}$$

Using this formula with eq. 19-11 gives

$$-\left(\frac{2\alpha}{\pi}\right)^{3/2}(4\pi)\int_0^\infty re^{-2\alpha r^2}\,dr = -\left(\frac{2\alpha}{\pi}\right)^{3/2}(4\pi)\left(\frac{0!}{2\cdot 2\alpha}\right)$$

$$= -2\left(\frac{2\alpha}{\pi}\right)^{1/2} \tag{19-13}$$

Putting it all together and taking the derivative with respect to α provides

$$\frac{d}{d\alpha}\left[\langle\psi_{1s}(r,\theta,\phi;\alpha)|H|\psi_{1s}(r,\theta,\phi;\alpha)\rangle\right] = \frac{3}{2} - \left(\frac{2}{\pi\alpha}\right)^{1/2} \tag{19-14}$$

This is equal to zero when $\alpha = 0.28294$. Using this value of α gives $<T> = 0.4244$ a.u. and $<V> = -0.8488$ a.u. (note that this satisfies the virial theorem, since $<V> = -2<T>$) and thus $<H> = -0.4244$ a.u. The exact answer is -0.5 a.u., of course, so the error is about 15%.

This is a fairly large error. The problem is that a Gaussian function is really rather different from a normal exponential. It fails to have a cusp at the nucleus, it fails to rise to as high an amplitude at the nucleus, and it drops off more rapidly as r gets large. The smaller amplitude near the nucleus (the positive charge attractor) reduces $<V>$. It also means the slope is smaller than in the exponential, so this reduces $<T>$, too, but since any effect on V is twice as big as on T by the virial theorem, the net effect is to reduce the magnitude of the binding energy.

Linear Combinations of Gaussians

While a single gaussian does not do as well as the exact wave function for H, what about a linear combination of two gaussians, one being "tighter" (i.e., more peaked near the nucleus) and one being "looser"? We then have

$$\psi_{1s}\left(r,\theta,\phi;c_1,\alpha_1,c_2,\alpha_2\right) = c_1\left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2} + c_2\left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2} \qquad (19\text{-}15)$$

We could treat both the c values and the α values all as variational coefficients, but that is a bit challenging for our purposes. Let's instead treat only the coefficients as variational parameters, and choose specific values for the two α exponents. In particular, we will choose $\alpha_1 = 1.0$ and $\alpha_2 = 0.2$.

Until we know the coefficients, we don't know the normalization, so we will have to evaluate not only $<T>$ and $<V>$ as above, but also $<\psi|\psi>$. Let's begin with the simplest evaluation, the overlap integral

$$\langle\psi_{1s}|\psi_{1s}\rangle = 4\pi \left[\begin{array}{l} c_1^2\left(\dfrac{2}{\pi}\right)^{3/2}\displaystyle\int_0^\infty e^{-2r^2}r^2dr \\[2ex] + 2c_1c_2\left(\dfrac{2}{\pi}\right)^{3/4}\left(\dfrac{0.4}{\pi}\right)^{3/4}\displaystyle\int_0^\infty e^{-1.2r^2}r^2dr \\[2ex] + c_2^2\left(\dfrac{0.4}{\pi}\right)^{3/2}\displaystyle\int_0^\infty e^{-0.4r^2}r^2dr \end{array} \right]$$

$$= 4\pi \left[\begin{array}{l} c_1^2\left(\dfrac{2}{\pi}\right)^{3/2}\left(\dfrac{1}{4\bullet 2}\right)\left(\dfrac{\pi}{2}\right)^{1/2} \\[2ex] + 2c_1c_2\left(\dfrac{2}{\pi}\right)^{3/4}\left(\dfrac{0.4}{\pi}\right)^{3/4}\left(\dfrac{1}{4\bullet 1.2}\right)\left(\dfrac{\pi}{1.2}\right)^{1/2} \\[2ex] + c_2^2\left(\dfrac{0.4}{\pi}\right)^{3/2}\left(\dfrac{1}{4\bullet 0.4}\right)\left(\dfrac{\pi}{0.4}\right)^{1/2} \end{array} \right] \qquad (19\text{-}16)$$

$$= c_1^2 + 1.2870c_1c_2 + c_2^2$$

In order to evaluate the remaining integrals, it is helpful to solve their generic forms and then plug in the appropriate values for α. For instance, for $<T>$ evaluated over two different gaussians we have

$$\left\langle \psi_{1s}(r,\theta,\phi;\alpha_1)\left|-\frac{1}{2}\nabla^2\right|\psi_{1s}(r,\theta,\phi;\alpha_2)\right\rangle$$

$$= -\frac{1}{2}\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\left(\frac{2\alpha_2}{\pi}\right)^{3/4}(4\pi)\int_0^\infty e^{-\alpha_1 r^2}\left(\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\right)e^{-\alpha_2 r^2}r^2dr$$

$$= 2\pi\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\left(6\alpha_2\int_0^\infty r^2 e^{-(\alpha_1+\alpha_2)r^2}dr - 4\alpha_2^2\int_0^\infty r^4 e^{-(\alpha_1+\alpha_2)r^2}dr\right)$$

$$= 2\pi\left(\frac{2\alpha_1}{\pi}\right)^{3/4}\left(\frac{2\alpha_2}{\pi}\right)^{3/4}\left\{6\alpha_2\left[\frac{1}{4(\alpha_1+\alpha_2)}\right] - 4\alpha_2^2\left[\frac{3}{8(\alpha_1+\alpha_2)^2}\right]\right\}\left(\frac{\pi}{\alpha_1+\alpha_2}\right)^{1/2}$$

$$= (2\alpha_1)^{3/4}(2\alpha_2)^{3/4}\left[\frac{3\alpha_1\alpha_2}{(\alpha_1+\alpha_2)^{5/2}}\right] \qquad (19\text{-}17)$$

Given our combination of two gaussians in each ψ, we will have four integrals that we might call (1,1), (1,0.2), (0.2,1) and (0.2,0.2) (note from the symmetry of eq. 19-17 that (1,0.2) and (0.2,1) must be equal—we could also have come to this conclusion from the turnover rule!). If we use eq. 19-17 and our chosen values for α we have

$$\left\langle \psi_{1s}\left|-\frac{1}{2}\nabla^2\right|\psi_{1s}\right\rangle = 1.5c_1^2 + 0.6435c_1c_2 + 0.3c_2^2 \qquad (19\text{-}18)$$

As a nice sanity check, note that the tighter gaussian (number 1, the one with the higher exponent) contributes the greater kinetic energy, because it has much more curvature.

Now let's turn to the nuclear attraction integrals. Again, it is simplest to solve the general case

$$\left\langle \psi_{1s}(r,\theta,\phi;\alpha_1) \left| -\frac{1}{r} \right| \psi_{1s}(r,\theta,\phi;\alpha_2) \right\rangle$$

$$= -\left(\frac{2\alpha_1}{\pi}\right)^{3/4} \left(\frac{2\alpha_2}{\pi}\right)^{3/4} (4\pi) \int_0^\infty e^{-\alpha_1 r^2} \left(\frac{1}{r}\right) e^{-\alpha_2 r^2} r^2 dr$$

$$= -\left(\frac{2\alpha_1}{\pi}\right)^{3/4} \left(\frac{2\alpha_2}{\pi}\right)^{3/4} (4\pi) \left(\int_0^\infty r e^{-(\alpha_1+\alpha_2)r^2} dr \right)$$

$$= -\left(\frac{2\alpha_1}{\pi}\right)^{3/4} \left(\frac{2\alpha_2}{\pi}\right)^{3/4} (4\pi) \left[\frac{1}{2(\alpha_1+\alpha_2)} \right]$$

$$= -(2\alpha_1)^{3/4} (2\alpha_2)^{3/4} \left[\frac{2}{\sqrt{\pi}(\alpha_1+\alpha_2)} \right] \tag{19-19}$$

Note again the symmetry of (1,2) and (2,1). The full evaluation using our chosen values for α gives

$$\left\langle \psi_{1s} \left| -\frac{1}{r} \right| \psi_{1s} \right\rangle = -1.5958c_1^2 - 1.5908c_1 c_2 - 0.7136c_2^2 \tag{19-20}$$

The sanity check here is that the terms involving gaussian 1 are more negative because this gaussian has larger amplitude near the nucleus.

So, we now have

$$\frac{\left\langle \psi_{1s}(r,\theta,\phi;c_1,\alpha_1,c_2,\alpha_2) | H | \psi_{1s}(r,\theta,\phi;c_1,\alpha_1,c_2,\alpha_2) \right\rangle}{\left\langle \psi_{1s}(r,\theta,\phi;c_1,\alpha_1,c_2,\alpha_2) | \psi_{1s}(r,\theta,\phi;c_1,\alpha_1,c_2,\alpha_2) \right\rangle} = -\frac{0.0958c_1^2 + 0.9473c_1 c_2 + 0.4136c_2^2}{c_1^2 + 1.2870c_1 c_2 + c_2^2}$$

$$\tag{19-21}$$

The variational coefficients are the c values, so we now take the derivative of eq. 19-21 with respect to each. We find that, irrespective of which derivative we take and set equal to zero, we end up with

$$0 = 0.8240c_1^2 + 0.6356c_1 c_2 - 0.4150c_2^2 \tag{19-22}$$

One equation in two unknowns does not allow us to determine values for both coefficients c. However, we also have the normalization requirement

$$\left\langle \psi_{1s} \middle| \psi_{1s} \right\rangle = c_1^2 + 1.2870c_1c_2 + c_2^2 = 1 \tag{19-23}$$

Now that we have two equations in two unknowns, we can solve to find $c_1 = 0.3221$ and $c_2 = 0.7621$. You can verify that this satisfies the normalization equation 19-23, and, if we plug these values into the expectation value for the Hamiltonian, we obtain an energy expectation value of –0.4827 a.u. Notice the enormous improvement over using a single gaussian function with an optimized exponent (which was –0.4244 a.u.)!

   In essence, we are using the gaussian functions as a *basis set* to describe the exact function. If we take more extensive linear combinations with different exponents, we would expect to continue to do better. Indeed, taking a linear combination of 3 gaussians with exponents α equal to 2.22766, 0.405771, and 0.109818 provides a final wave function for which *<H>* = –0.4950—the error is now down to 1%. The graph on the next page illustrates how closely the sum of the 3 gaussian functions fits the exact hydrogenic wave function. The optimized coefficients in the figure caption can be determined in precisely the same fashion used above, except that one must keep track of more terms. Verification of the coefficient values is left as an exercise for the interested reader...

Homework

To be solved in class:

Establish whether the virial theorem is satisfied for our optimized two-gaussian wave function.

To be turned in for possible grading Mar. 10:

Today's in-class homework solution showed that the expectation value of the momentum operator for any real wave function must be zero. Why doesn't the same proof hold for any complex wave function?
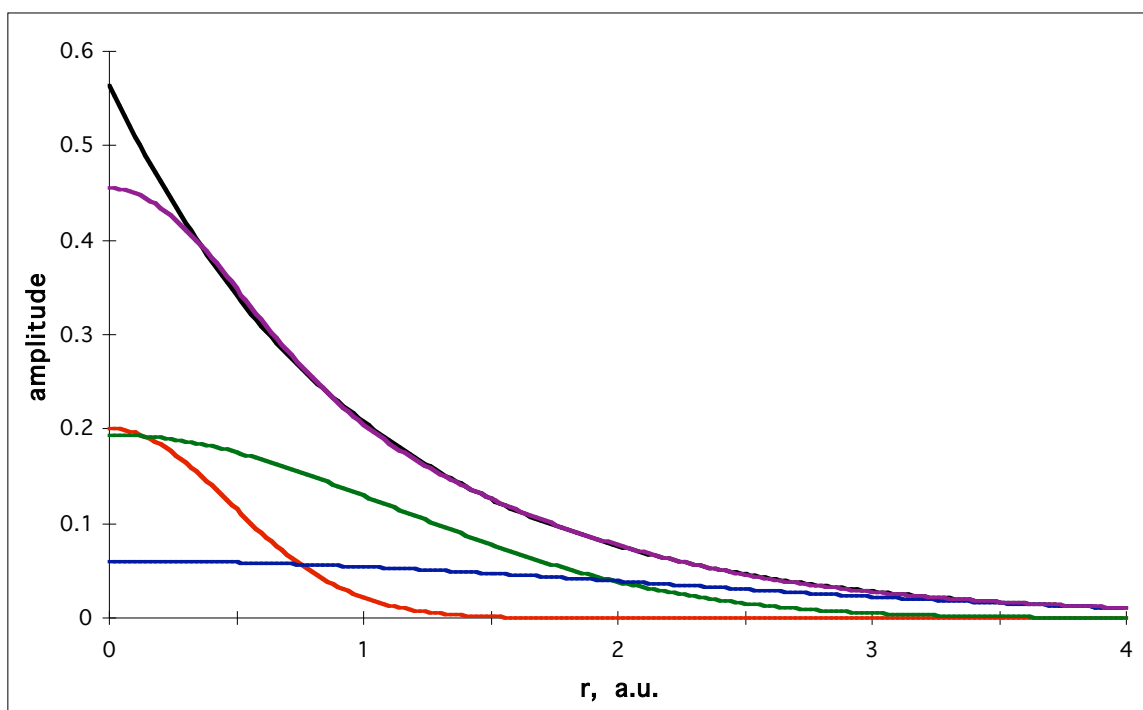
Figure Caption. The radial behavior of various basis functions in atom-centered coordinates. In black is the exact hydrogen 1s wave function. The purple curve is the optimized sum of a set of one each tight, medium, and loose gaussian functions shown in red, green, and blue, respectively. The respective gaussian exponents α are 2.227660, 0.405771, and 0.109818, and the associated contraction coefficients c are 0.14725, 0.53266, and 0.45233. Note that from 0.5 to 4.0 a.u., the linear-combination wave function matches the exact one closely. However, near the origin there is a notable difference and, were the plot to extend to very large r, it would be apparent that the decay of the linear-combination wave function is more rapid than the exact one.