

# Engel 10.9

**Problem.** Use the variation method to optimize a model wave function for a one-electron atom. The model wave function is  $e^{-\alpha r}$  where  $\alpha$  is the so-called "variational parameter". The idea is to adjust  $\alpha$  to make the energy as low as possible.

**Answer.** The instructions are straightforward (I hope).

**a.** Determine the value of  $\hat{H} \Phi$ . The Hamiltonian consists of two pieces, a kinetic energy operator and a Coulomb energy operator. The Coulomb operator is multiplied by the wave function, so I will accept Engel's result as a given. The kinetic energy operator involves differentiation, but is easily simplified as shown below. I begin by defining the wave function, taking its derivative with respect to  $r$ , and multiplying the result by  $r^2$  ...

```
Clear[phi, hbar, me, alpha, KE]
phi = e^{-alpha r}
KE = D_r phi
KE = r^2 KE

e^{-r alpha}
-e^{-r alpha} alpha
-e^{-r alpha} r^2 alpha
```

I differentiate the last result again with respect to  $r$ , and use the product rule ...

```
KE = D_r KE
-2 e^{-r alpha} r alpha + e^{-r alpha} r^2 alpha^2
```

Finally, I divide the last result by  $r^2$  and multiply by some constants ...

```
KE = Simplify[ -hbar^2 / (2 me r^2) KE ]
- (e^{-r alpha} hbar^2 alpha (-2 + r alpha)) / (2 me r)
```

This result is equivalent to Engel's, and when combined with the Coulomb term, gives  $\hat{H} \Phi$

**b.** Engel's integral formulas contain two equalities. The first one replaces an integral over all coordinates with an integral over  $r$  only. A factor of  $4\pi$  replaces the two integrals over angular coordinates,  $\theta$  and  $\phi$ , and it is easy to see where this factor comes from ...

$$\left( \int_0^\pi \sin[\mathbf{x}] \, d\mathbf{x} \right) \left( \int_0^{2\pi} d\mathbf{y} \right)$$

4  $\pi$

The second equality requires us to evaluate the integral of  $r^2 \Phi \hat{H} \Phi$ . Part **a** gave us  $\hat{H} \Phi$  and the rest of the integrand is obtained by multiplication:

```

Clear[f]
f = r^2 phi (KE - (qe^2 / (4 pi epsilon_0 r)) phi)
e^{-r alpha} r^2 ( - (e^{-r alpha} hbar^2 alpha (-2 + r alpha) / (2 m epsilon_0 r)) - (e^{-r alpha} qe^2 / (4 pi r epsilon_0)) )

FullSimplify[4 pi f]
- (e^{-2 r alpha} r (m e qe^2 + 2 hbar^2 pi alpha (-2 + r alpha) epsilon_0) / (m epsilon_0))

Integrate[% dr, {r, 0, infinity}]
If[Re[alpha] > 0, - (m e qe^2 - 2 hbar^2 pi alpha epsilon_0) / (4 m alpha^2 epsilon_0),
Integrate[- (e^{-2 r alpha} r (m e qe^2 + 2 hbar^2 pi alpha (-2 + r alpha) epsilon_0) / (m epsilon_0)), {r, 0, infinity}, Assumptions -> Re[alpha] <= 0]]

f = FullSimplify[% , alpha > 0]
- (m e qe^2 - 2 hbar^2 pi alpha epsilon_0) / (4 m alpha^2 epsilon_0)

```

This result is equivalent to the formula given in Engel.

**c.** The two equalities show how to evaluate the denominator of the expectation value formula. As described in part **b**, the factor of  $4\pi$  appears because of the integrals over angular coordinates. The integral with respect to  $r$  can be evaluated as follows

```

g = r^2 phi^2
e^{-2 r alpha} r^2

Integrate[g dr, {r, 0, infinity}]
If[Re[alpha] > 0, 1 / (4 alpha^3), Integrate[e^{-2 r alpha} r^2, {r, 0, infinity}, Assumptions -> Re[alpha] <= 0]]

g = FullSimplify[4 pi %, alpha > 0]
pi / alpha^3

```

This is identical to Engel's formula.

**d.** The next step is to combine the numerator and denominator and obtain a formula for the expectation value of the energy that depends on the variational parameter  $\alpha$ .

```
Clear[Energy]
```

```
Energy = f / g
```

$$-\frac{\alpha (m e q e^2 - 2 \hbar^2 \pi \alpha \epsilon_0)}{4 m e \pi \epsilon_0}$$

This is equivalent to Engel's formula. Our goal is to adjust the variational parameter so that this energy is minimized. This is done in the usual way by finding a value of  $\alpha$  that makes the derivative  $dE/d\alpha$  vanish.

```
Clear[DE]
```

```
DE = D[Energy, \alpha]
```

$$\frac{\hbar^2 \alpha}{2 m e} - \frac{m e q e^2 - 2 \hbar^2 \pi \alpha \epsilon_0}{4 m e \pi \epsilon_0}$$

Now it's just algebra, but we can also use *Mathematica's* Solve function.

```
Clear[\alphaopt]
```

```
\alphaopt = Solve[DE == 0, \alpha]
```

$$\left\{ \left\{ \alpha \rightarrow \frac{m e q e^2}{4 \hbar^2 \pi \epsilon_0} \right\} \right\}$$

Recall that our model wave function is an approximation to the  $1s$  wave function of hydrogen. The formula for this wave function is given on Engel p. 164 and it shows that the function's exponent is  $-r/a_0$ . This suggests that we might get some insight by converting our optimized variational parameter into a multiple of  $a_0$ .

Engel p. 163 gives a formula for  $a_0$  that can be rewritten as follows:

$$\frac{1}{a_0} = \frac{\pi m e q e^2}{\epsilon_0 \hbar^2} = \frac{\pi m e q e^2}{\epsilon_0 (2 \pi \hbar)^2} = \frac{m e q e^2}{\epsilon_0 4 \pi \hbar^2}$$

The optimized variational parameter is identical to  $1/a_0$ . In other words, 1) the variationally optimized wave function is identical to the  $1s$  wave function, and 2) the variational wave function must have the same energy as the true wave function.

e. Another way to evaluate the variationally optimized energy is to substitute the optimized variational parameter back into the energy formula. I won't do this because of the preceding discussion. However, if you followed this route, you should have found that the variationally optimized energy was identical to the true energy.