

# Chemistry 3730 Fall 2002 Test 3 Solutions

1. There are two methods to calculate the ionization energy:

- (a) Arsenic has a  $p^3$  outer-shell configuration. Its ground-state spin multiplicity is therefore 4. I performed an unrestricted Hartree-Fock calculation with the 6-311G\* basis set and obtained an energy of  $-1401953.013947$  kcal/mol. The relevant ion has a charge of +1 and a spin multiplicity of 3. A similar *ab initio* calculation to that used for the atom gives a ground-state energy of  $-1401734.982284$  kcal/mol. The ionization energy is therefore

$$IE = -1401734.982284 - (-1401953.013947 \text{ kcal/mol}) = 218.031663 \text{ kcal/mol.}$$

Applying the conversion factor, this is 9.4548 eV.

To really do this right, we should also consider the correlation energy which we can calculate using the MP2 method. We haven't learned about this yet, but for the record, the corrected energies are  $-1402232.876553$  and  $-1402005.193477$  kcal/mol for the atom and ion, respectively. The ionization energy is then 227.683076 kcal/mol, or 9.8733 eV.

- (b) The other (simpler) alternative is to use Koopmans's theorem. From the *ab initio* calculation described above, we find that the orbital energy for the last occupied orbital is  $-10.01578$  eV. The ionization energy is therefore 10.01578 eV.

The experimental ionization energy is 9.815 eV.

2. (a) By writing orbital occupancies such as  $1s^2$ , we are assuming that we can describe the wavefunction of a many-electron system using one-electron orbitals. In other words, we are assuming that the wavefunction can be represented without terms involving the relative positions of the two electrons. This is only true if the two electrons don't interact which, of course, they do. In perturbation theory, we treat the electron repulsion term as small and find that the zero-order problem consists of two electrons in a  $1s$  orbital. The  $1s^2$  description can therefore be thought of as being a first approximation based on perturbation theory for the ground state of a helium atom.
- (b) In order to use the variational method to calculate an excited state, we must have trial wavefunctions which are orthogonal to any states which are lower in energy. However, we don't know the wavefunctions of any of the states (or we wouldn't be using the variational method). Accordingly, the best we can do is to build trial wavefunctions which are orthogonal to the variational approximations to the lower states. Except for the first excited state where wavefunction symmetry requirements often simplify this problem, orthogonality to a set of approximate solutions does not guarantee orthogonality to the exact solutions.

3. (a) There are two quite different ways to go about answering this question:
- i.

$$\begin{aligned}\langle \psi_1 | \psi_0 \rangle &= \langle \phi_1(1,2) \alpha(1) \alpha(2) | \phi_1(1,2) \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) + \alpha(2) \beta(1)] \rangle \\ &= \frac{1}{\sqrt{2}} \langle \phi_1 | \phi_1 \rangle \langle \alpha(1) \alpha(2) | \alpha(1) \beta(2) + \alpha(2) \beta(1) \rangle.\end{aligned}$$

Because the spatial part of the wavefunction ( $\phi_1$ ) is normalized, the inner product  $\langle \phi_1 | \phi_1 \rangle = 1$ . Therefore

$$\begin{aligned}\langle \psi_1 | \psi_0 \rangle &= \frac{1}{\sqrt{2}} [\langle \alpha(1) \alpha(2) | \alpha(1) \beta(2) \rangle + \langle \alpha(1) \alpha(2) | \alpha(2) \beta(1) \rangle] \\ &= \frac{1}{\sqrt{2}} [\langle \alpha(1) | \alpha(1) \rangle \langle \alpha(2) | \beta(2) \rangle + \langle \alpha(1) | \beta(1) \rangle \langle \alpha(2) | \alpha(2) \rangle].\end{aligned}$$

But  $\langle \alpha(i) | \beta(i) \rangle = 0$ .

$\therefore \langle \psi_1 | \psi_0 \rangle = 0$ .

- ii.  $\psi_1$  and  $\psi_0$  are eigenfunctions of the Hermitian operator  $\hat{S}_z$  corresponding to different eigenvalues. They must therefore be orthogonal.

(b) We want

$$\begin{aligned}\langle \psi_{11(-1)} | \psi_{11(-1)} \rangle &= 1. \\ \langle \psi_{11(-1)} | \psi_{11(-1)} \rangle &= N^2 \langle \psi_1 + \psi_0 - \psi_{-1} | \psi_1 + \psi_0 - \psi_{-1} \rangle \\ &= N^2 [\langle \psi_1 | \psi_1 \rangle + \langle \psi_0 | \psi_0 \rangle + \langle \psi_{-1} | \psi_{-1} \rangle].\end{aligned}$$

Note that all of the terms which are zero due to the orthogonality of the spin-orbitals were discarded in obtaining the last equality. Furthermore, since the individual spin-orbitals are normalized,

$$\begin{aligned}\langle \psi_{11(-1)} | \psi_{11(-1)} \rangle &= 3N^2 = 1. \\ \therefore N &= \frac{1}{\sqrt{3}}.\end{aligned}$$

- (c)  $\psi_{11(-1)}$  is a linear combination of functions which are eigenfunctions of  $\hat{S}^2$ , each with an eigenvalue of  $2\hbar^2$ . Accordingly,  $\psi_{11(-1)}$  is also an eigenfunction of  $\hat{S}^2$  with eigenvalue  $2\hbar^2$ . If you prefer a formal demonstration, here it is:

$$\begin{aligned}\hat{S}^2 \psi_{11(-1)} &= \frac{1}{\sqrt{3}} \hat{S}^2 (\psi_1 + \psi_0 - \psi_{-1}) \\ &= \frac{1}{\sqrt{3}} (\hat{S}^2 \psi_1 + \hat{S}^2 \psi_0 - \hat{S}^2 \psi_{-1})\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{\sqrt{3}} (2\hbar^2\psi_1 + 2\hbar^2\psi_0 - 2\hbar^2\psi_{-1}) \\
&= 2\hbar^2 \frac{1}{\sqrt{3}} (\psi_1 + \psi_0 - \psi_{-1}) \\
&= 2\hbar^2 \psi_{11(-1)}.
\end{aligned}$$

(d)

$$\begin{aligned}
\hat{S}_z \psi_{11(-1)} &= \frac{1}{\sqrt{3}} \hat{S}_z (\psi_1 + \psi_0 - \psi_{-1}) \\
&= \frac{1}{\sqrt{3}} (\hat{S}_z \psi_1 + \hat{S}_z \psi_0 - \hat{S}_z \psi_{-1}) \\
&= \frac{1}{\sqrt{3}} (\hbar\psi_1 + 0\hbar\psi_0 - (-1)\hbar\psi_{-1}) \\
&= \hbar \frac{1}{\sqrt{3}} (\psi_1 + \psi_{-1}) \\
&\neq M_S \hbar \psi_{11(-1)}.
\end{aligned}$$

$\psi_{11(-1)}$  is not an eigenfunction of  $\hat{S}_z$ .

**Bonus question:** Let our new wavefunction be

$$\psi_{\text{new}} = A (\psi_1 + a\psi_0 + b\psi_{-1}).$$

where  $a$  and  $b$  and  $A$  are constants to be determined. The normalization of  $\psi_{\text{new}}$  gives

$$A = 1/\sqrt{1+a^2+b^2}.$$

If  $\psi_{\text{new}}$  is orthogonal to  $\psi_{11(-1)}$ , then

$$\begin{aligned}
\langle \psi_{11(-1)} | \psi_{\text{new}} \rangle &= 0. \\
\langle \psi_{11(-1)} | \psi_{\text{new}} \rangle &= \frac{A}{\sqrt{3}} \langle \psi_1 + \psi_0 - \psi_{-1} | \psi_1 + a\psi_0 + b\psi_{-1} \rangle \\
&= \frac{A}{\sqrt{3}} (1 + a + b). \\
\therefore 1 + a - b &= 0.
\end{aligned}$$

We can choose any two numbers  $a$  and  $b$  which satisfy this relation. For instance,  $a = \frac{2}{3}$ ,  $b = \frac{5}{3}$  would work. This would give us the wavefunction

$$\psi_{1\frac{2}{3}\frac{5}{3}} = \frac{3}{\sqrt{38}} \left( \psi_1 + \frac{2}{3}\psi_0 + \frac{5}{3}\psi_{-1} \right).$$

4. We start by defining the variational wavefunction:

```
> phi := x -> exp(-b*x^2);
```

$$\phi := x \rightarrow e^{(-bx^2)}$$

```
> assume(b>0);
```

The variational energy is

$$E^{\text{var}} = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\langle \phi | \hat{K} | \phi \rangle + \langle \phi | \hat{V} | \phi \rangle}{\langle \phi | \phi \rangle}.$$

We can evaluate this expression in pieces using Maple:

```
> Kip := -hbar^2/(2*m)*int(phi(x)*diff(phi(x),x$2),
  x=-infinity..infinity);
```

$$Kip := \frac{1}{4} \frac{\hbar^2 \sqrt{b} \sqrt{2} \sqrt{\pi}}{m}$$

```
> V := x -> A*abs(x);
```

$$V := x \rightarrow A |x|$$

```
> Vip := int(phi(x)^2*V(x),x=-infinity..infinity);
```

$$Vip := \frac{1}{2} \frac{A}{b}$$

```
> ip := int(phi(x)^2,x=-infinity..infinity);
```

$$ip := \frac{1}{2} \frac{\sqrt{2} \sqrt{\pi}}{\sqrt{b}}$$

```
> Evar := (Kip+Vip)/ip;
```

```
> soln:=solve(diff(Evar,b)=0,b);
```

$$\begin{aligned}
\text{soln} &:= \frac{1}{4} \frac{4^{(2/3)} \left(\frac{\sqrt{2} A m \hbar}{\sqrt{\pi}}\right)^{(2/3)}}{\hbar^2}, \\
&\left( \frac{-\frac{1}{4} \frac{4^{(1/3)} \left(\frac{\sqrt{2} A m \hbar}{\sqrt{\pi}}\right)^{(1/3)}}{\hbar} + \frac{1}{4} I \sqrt{3} 4^{(1/3)} \left(\frac{\sqrt{2} A m \hbar}{\sqrt{\pi}}\right)^{(1/3)}}{\hbar} \right)^2, \\
&\left( \frac{-\frac{1}{4} \frac{4^{(1/3)} \left(\frac{\sqrt{2} A m \hbar}{\sqrt{\pi}}\right)^{(1/3)}}{\hbar} - \frac{1}{4} I \sqrt{3} 4^{(1/3)} \left(\frac{\sqrt{2} A m \hbar}{\sqrt{\pi}}\right)^{(1/3)}}{\hbar} \right)^2
\end{aligned}$$

The first solution is the correct one. When we started this problem, we assumed that  $b > 0$ , which implies that  $b$  is real. The complex solutions we're getting now contradict this assumption and so must be rejected. We obtain the energy by substituting the first result into the energy:

```

> assume(m>0);
> assume(hbar>0);
> assume(A>0);
> Emin := simplify(subs(b=soln[1],Evar));

```

$$E_{\min} := \frac{3}{4} \frac{\hbar^{-(2/3)} A^{-(2/3)} 2^{(2/3)}}{m^{(1/3)} \pi^{(1/3)}}$$

**Bonus question** The wavefunction for the first excited state should be orthogonal to the ground-state wavefunction. Try

```

> phi1 := x -> x*exp(-f*x^2);

```

$$\phi_1 := x \rightarrow x e^{-f x^2}$$

where  $f$  is a positive variational parameter.

```

> assume(f>0);

```

Let's test for orthogonality:

```

> int(phi(x)*phi1(x),x=-infinity..infinity);

```

0

The wavefunction should also obey the boundary conditions and be square-integrable:

> limit(phi1(x),x=infinity);

0

> limit(phi1(x),x=-infinity);

0

> ip := int(phi1(x)^2,x=-infinity..infinity);

$$ip := \frac{1}{8} \frac{\sqrt{2}\sqrt{\pi}}{f^{(3/2)}}$$

Now that we know that our wavefunction is sensible, all we have to do is apply the variational method:

> Kip := -hbar^2/(2\*m)\*int(phi1(x)\*diff(phi1(x),x\$2),  
x=-infinity..infinity);

$$Kip := \frac{3}{16} \frac{hbar^2 \sqrt{2}\sqrt{\pi}}{m \sqrt{f}}$$

> Vip := int(phi1(x)^2\*V(x),x=-infinity..infinity);

$$Vip := \frac{1}{4} \frac{A}{f^2}$$

> Evar1 := (Kip+Vip)/ip:

> soln1:=solve(diff(Evar1,f)=0,f);

$$soln1 := \frac{1}{9} \frac{9^{(2/3)} \left( \frac{\sqrt{2} A \tilde{m} \hbar}{\sqrt{\pi}} \right)^{(2/3)}}{\hbar^2},$$

$$\left( -\frac{1}{6} \frac{9^{(1/3)} \left( \frac{\sqrt{2} A \tilde{m} \hbar}{\sqrt{\pi}} \right)^{(1/3)}}{\hbar} + \frac{1}{6} I \sqrt{3} 9^{(1/3)} \left( \frac{\sqrt{2} A \tilde{m} \hbar}{\sqrt{\pi}} \right)^{(1/3)} \right)^2,$$

$$\left( -\frac{1}{6} \frac{9^{(1/3)} \left( \frac{\sqrt{2} A \tilde{m} \hbar}{\sqrt{\pi}} \right)^{(1/3)}}{\hbar} - \frac{1}{6} I \sqrt{3} 9^{(1/3)} \left( \frac{\sqrt{2} A \tilde{m} \hbar}{\sqrt{\pi}} \right)^{(1/3)} \right)^2$$

Again, the only sensible solution is the first one. Thus the energy is

```
> simplify(subs(f=soln1[1],Evar1));
```

$$\frac{3 \hbar^{2/3} 3^{1/3} 2^{1/3} A^{2/3}}{2 m^{1/3} \pi^{1/3}}$$

5. The expectation value is calculated by  $\langle K \rangle = \langle \Psi_{2p_0} | \hat{K} | \Psi_{2p_0} \rangle$ . For simplicity, define the radial part of the kinetic energy operator

$$\hat{K} = -\frac{1}{2r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$$

such that

$$\hat{K} = \hat{K} + \frac{1}{2r^2} \hat{L}^2.$$

The expression to evaluate is

$$\langle K \rangle = \langle \Psi_{2p_0} | \hat{K} | \Psi_{2p_0} \rangle + \langle \Psi_{2p_0} | \frac{1}{2r^2} \hat{L}^2 | \Psi_{2p_0} \rangle.$$

But  $\hat{L}^2 | \Psi_{2p_0} \rangle = \ell(\ell+1) | \Psi_{2p_0} \rangle = 1(1+1) | \Psi_{2p_0} \rangle = 2 | \Psi_{2p_0} \rangle$ .

$$\therefore \langle K \rangle = \langle \Psi_{2p_0} | \hat{K} | \Psi_{2p_0} \rangle + \langle \Psi_{2p_0} | \frac{1}{r^2} | \Psi_{2p_0} \rangle.$$

Since  $Z = 1$ ,

$$\begin{aligned} \langle K \rangle &= -\frac{1}{32\pi} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} r e^{-r/2} \frac{1}{2r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} (r e^{-r/2}) \right) \cos^2 \theta r^2 \sin \theta dr d\theta d\phi \\ &\quad + \frac{1}{32\pi} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} (r e^{-r/2} \cos \theta)^2 \frac{1}{r^2} r^2 \sin \theta dr d\theta d\phi \\ &= -\frac{1}{64\pi} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} r e^{-r/2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} (r e^{-r/2}) \right) \cos^2 \theta \sin \theta dr d\theta d\phi \\ &\quad + \frac{1}{32\pi} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} r^2 e^{-r} \cos^2 \theta \sin \theta dr d\theta d\phi \\ &= -\frac{1}{32} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} r e^{-r/2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} (r e^{-r/2}) \right) \cos^2 \theta \sin \theta dr d\theta \\ &\quad + \frac{1}{16} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} r^2 e^{-r} \cos^2 \theta \sin \theta dr d\theta \end{aligned}$$

We can now use Maple to do the rest:

```
> i1 := -1/32*int(int(r*exp(-r/2)*diff(r^2*diff(r*exp(-r/2),r),r)
*cos(theta)^2*sin(theta),r=0..infinity),theta=0..Pi);
```

$$i1 := \frac{1}{24}$$

```
> i2 := 1/16*int(int(r^2*exp(-r)*cos(theta)^2*sin(theta),r=0..infinity),  
theta=0..Pi);
```

$$i2 := \frac{1}{12}$$

```
> avg_K := i1+i2;
```

$$avg\_K := \frac{1}{8}$$

The average kinetic energy is therefore  $\frac{1}{8}$  hartree.