Chem. 231B Homework 2 Solutions

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22.4.

1. \[ T = V = \frac{1}{2} E \]

2. For a real atom, \[ \hat{V} = \hat{V}_{ee} + \hat{V}_{en} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \frac{Z_i}{r_i^2} \]

\[ 2\langle \hat{T} \rangle = \langle \sum_i \mathbf{r}_i \cdot \nabla_i \hat{V} \rangle \]

\[ = \sum_i \mathbf{r}_i \cdot \left( \frac{\mathbf{r}_j - \mathbf{r}_i}{|\mathbf{r}_i - \mathbf{r}_j|^3} + Z \sum_i \frac{\mathbf{r}_i \cdot \mathbf{r}_i}{r_i^3} \right) \]

\[ = \left( -\sum_{i \neq j} \frac{\mathbf{r}_i^2 - \mathbf{r}_i \cdot \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|^3} - Z \sum_i \frac{1}{r_i} \right) \]

\[ = \left( -\sum_{j>i} \frac{\mathbf{r}_i^2 - 2 \mathbf{r}_i \cdot \mathbf{r}_j + r_j^2}{|\mathbf{r}_i - \mathbf{r}_j|^3} \right) - \langle V_{en} \rangle \]

\[ = -\langle \hat{V}_{ee} \rangle - \langle \hat{V}_{en} \rangle \quad (1) \]

For Hydrogen, \[ \hat{V}_{ee} = 0 \] so \[ 2T = -V. \]

3. Nuclear cusp condition is that \[ \frac{\partial n}{\partial r} \bigg|_{r=0} = -2Zn(0). \] For Hydrogen, \( Z = 1 \) and the ground-state density is \( n(r) = \frac{1}{2} e^{-\alpha r}. \)

\[ \frac{\partial n}{\partial r} \bigg|_{r=0} = -2Zn(0) = -\frac{2}{\pi} \quad (2) \]

4. The figure gives approximately \[ \frac{\partial n}{\partial r} \bigg|_{r=0} \approx 2.5-3.6 = 0.1-0 \]

-11 and \( -2Zn(0) \approx -2(2)(3.6) = -14.4. \)

5. Ionization potential theorem states that \[ \sqrt{n(r)} \sim e^{-\alpha r}, \] where \( \alpha = \sqrt{2I} \) and \( I = E(N-1) - E(N). \) For Hydrogen, \( I = \frac{1}{2} \Rightarrow \alpha = 1 \) and \[ \sqrt{n(r)} = \frac{1}{2} e^{-r}. \]

6. The logarithmic density will be almost linear, with a negative slope and a y-intercept of \( \ln n(0). \) A sketch is shown in Figure 1. In the limit \( r \to \infty, \) the ionization potential theorem predicts that \( \sqrt{n(r)} \sim e^{-\alpha r} \Rightarrow \ln n(r) = -2r\sqrt{2I}, \) so the logarithm of the density will be linear with a slope of \(-2\sqrt{2I}. \) For small \( r, \) the nuclear cusp condition states that \( \frac{\partial n}{\partial r} \bigg|_{r=0} = -2Zn(0). \) We can integrate to get \( n(r) = n(0) - 2Zn(0)r. \) Taking the logarithm we get

\[ \ln n(r) = \ln[n(0)(1 - 2Zr)] \]

\[ = \ln n(0) + \ln(1 - 2Zr) \]

\[ \approx \ln n(0) - 2Zr \quad (3) \]

by expanding the logarithm for small \( r. \) Thus in this limit the logarithmic density is also linear, with a slope of \(-2Z. \)

FIG. 1 A sketch of the logarithmic density. Red is in the limit of small \( r \) and black is in the limit of large \( r. \) The dashed regions are unknown.

Just a note: if we consider Helium with non-interacting electrons, which is solvable and whose density is \( n(r) = \frac{8}{\pi e^{-4r}}, \) then the logarithmic density is \( \ln n(r) = \ln(n(\frac{2}{3}) - 4r. \) This is linear with a constant negative slope of \(-4. \)

With no electron-electron interaction, the ionization potential is \( I = 2 \) and \(-2\sqrt{2I} = -2Z = -4. \) Thus the cusp condition and the ionization potential theorem give the same exact answer in this case.

22.5.

1. The exact energy is \( E = -\frac{1}{2}. \) Using \( \phi_G(r) = \frac{1}{\pi^{3/2}} \exp(-r^2/2) \) as a trial wavefunction, we get \( T = \frac{3}{4}, \)
\( V = -\frac{2}{\sigma^2} \) and a total energy of \( E = \frac{3}{4} - \frac{2}{\sqrt{3}} \approx -0.38 \) (24\% error). This satisfies variational (since we used the full Hamiltonian), but not virial (since our estimate is bad): \( V/T = -1.5 \neq -2 \).

2.

Using \( \phi(r) = \frac{5}{\sqrt{2\pi}} \exp(-\frac{a^2}{8}) \), we get \( T = \frac{3a^2}{4} \), \( V = -\frac{2\sqrt{2\pi}}{a} \) and a total energy of \( E = \frac{3a^2}{4} - \frac{2\sqrt{2\pi}}{a} \). Minimizing w.r.t. \( a \) gives \( a = \frac{16}{9\pi} \) and \( E = -0.42 \) (16\% error). This is a slightly better result. Both variational and virial are satisfied (virial is always satisfied when using a variational parameter that multiplies \( x \) or \( r \)):

\[ V/T = -2. \]

3.

Using \( \phi_1(r) = \exp(-\frac{r^2}{4}) \) and \( \phi_2(r) = \exp(-2r^2) \), construct the Hamiltonian and overlap matrices

\[
H = \begin{bmatrix}
\frac{3}{4} & -\frac{16}{\sqrt{\pi}} \\
\frac{16}{\sqrt{\pi}} & -\frac{9}{4}
\end{bmatrix}
\]

\[ S = \begin{bmatrix}
2\sqrt{2\pi} & 8\pi^{3/2}/27 \\
8\pi^{3/2}/27 & \pi^{3/2}/8
\end{bmatrix}
\]

We seek solutions to the equation \( Hv = cSv \). We can either solve \(|H - cS| = 0\) or equivalently solve for the eigenvalues and eigenvectors of \( S^{-1}H \) (which is easy in Mathematica). The total energy is -0.483 and the coefficients are 0.224 and 0.235 for \( \phi_1 \) and \( \phi_2 \), respectively, after normalization.

4.

This is a better estimate. It is variational and although it does not satisfy virial, it is closer than before (which means that our estimate is better).

5.

Figure 2 shows the exact wavefunction and the four trial wavefunctions from parts (1), (2), (3) and (6). Note that even though (2) gives a better total energy than (1), its wavefunction is worse. Cusp condition not satisfied since we are using Gaussians \( \left( \frac{\partial}{\partial r} \right)_{r=0} = 0 \). Ionization potential theorem is also not satisfied since \( e^{-\alpha r^2} \) decays too fast compared to \( e^{-\alpha r} \).

6.

The most general form of the wavefunction using two Gaussians is

\[ \phi(r) = A\phi_a(r) + B\phi_b(r) \]

\[ \phi_a(r) = \left( \frac{a}{\pi} \right)^{3/4} \exp(-\frac{a^2 r^2}{8}). \] The general expression for the total energy is

\[
E = \frac{3}{4}(aA^2 + bB^2) - \frac{2}{\sqrt{\pi}}(\sqrt{a}A^2 + \sqrt{b}B^2)
\]

\[
- \frac{8AB(ab)^{3/4}}{(a + b)^{3/2}} + \frac{6\sqrt{2AB(ab)^{7/4}}}{(a + b)^{5/2}}
\]

We do a full minimization of \( E \) w.r.t. all 4 parameters, subject to the constraint that the wavefunction remains normalized

\[
A^2 + B^2 + \frac{4\sqrt{2}AB(ab)^{3/4}}{(a + b)^{3/2}} = 1
\]

Using the values for the 4 parameters found previously as an initial guess, we find that the minimized values are \( A = 0.821, B = 0.274, a = 0.403 \) and \( b = 2.66 \). The minimum energy is \( E = -0.486 \). The answers to the previous 2 questions remain the same, although the estimate is slightly better than before.

22.6.

1.

Box eigenvalues and eigenfunctions are \( \epsilon_j = \frac{n^2 \pi^2}{2} \) and \( \phi_j(x) = \sqrt{2} \sin(j \pi x) \). (Note: in the problem \( a = 1 \) but here I assume \( a = 1 \) in AU). Both electrons occupy the first orbital, so the spin part is antisymmetric while the spatial part is symmetric.

\[
\Psi(1, 2) = \chi_{\text{singlet}} \phi_1(1) \phi_1(2)
\]

\[
= \frac{1}{\sqrt{2}}(\chi_{\uparrow 1} - \chi_{\downarrow 1})\phi_1(1)\phi_1(2)
\]

Total energy is \( E = 2\epsilon_1 = \pi^2 \).
2.

The proper way to derive this is to use the definition of the one-electron density

\[
n(x) = N \int dx_2 \ldots \int dx_N |\Psi(x, x_2, \ldots, x_N)|^2
\]

(11)

In this case

\[
n(x) = 2 \int dx_2 \sin^2(\pi x)2 \sin^2(\pi x_2)
\]

(12)

\[
= 4 \sin^2(\pi x)
\]

(13)

We could also use the fact the our wavefunction is a Slater determinant, which implies that the density must be the sum of the squares of the occupied orbitals.

3.

\[
\epsilon_{HOMO} = \frac{\pi^2}{2}
\]

and \(\epsilon_{LUMO} = 2\pi^2\). \(I = E_N - E_{N-1} = \pi^2/2\) and \(A = E_{N+1} - E_N = 2\pi^2\).

4.

Least energy needed to excite the system is \(\epsilon_{LUMO} - \epsilon_{HOMO} = \frac{3}{2}\pi^2\), which is negative the HOMO-LUMO gap. The fundamental gap is \(I - A = -\frac{3}{2}\pi^2\), which is the same as the HOMO-LUMO gap.

5.

Start from a Slater determinant

\[
\psi(1, 2, 3) = \frac{1}{\sqrt{6}} \begin{vmatrix}
\phi_1(1)\alpha_1(1) & \phi_1(2)\alpha_1(2) & \phi_1(3)\alpha_1(3) \\
\phi_1(1)\alpha_2(1) & \phi_1(2)\alpha_2(2) & \phi_1(3)\alpha_2(3) \\
\phi_2(1)\alpha_1(1) & \phi_2(2)\alpha_1(2) & \phi_2(3)\alpha_2(3)
\end{vmatrix}
\]

(14)

where \(\alpha_1 = \uparrow\) and \(\alpha_2 = \downarrow\). If we let \(\phi(1, 2) = \phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)\), then

\[
\psi(1, 2, 3) = \phi_1(1)\phi^2(3, 2)|\uparrow\uparrow\uparrow| + \phi_1(2)\phi^2(1, 3)|\uparrow\uparrow\downarrow| + \phi_1(3)\phi^2(2, 1)|\uparrow\downarrow\downarrow|
\]

(15)

(16)

(17)

A single-particle operator is \(\hat{A} = \sum_{i=1}^3 \hat{a}_i\). For a Slater determinant, \(\langle \hat{A} \rangle = 3\langle \hat{a} \rangle\). Since there is a \(\frac{2}{3}\) chance the particle will be in \(\phi_1\) and a \(\frac{1}{3}\) chance it will be in \(\phi_2\), the expectation value is

\[
\langle \hat{A} \rangle = 2 \int dx \phi_1^*(x)\hat{a}\phi_1(x) + 3 \int dx \phi_2^*(x)\hat{a}\phi_2(x)
\]

(18)

6.

Including weak electron-electron repulsion, the ground state energy will increase slightly. Orbitals do not mean much in this case, but if you really wanted to write the wavefunction, you would need an infinite sum of Slater determinants of all excited states. The ground-state density will smear out a little bit, due to the repulsion between the electrons. \(I\) should decrease, since due to the repulsion it should be easier to remove an electron. \(A\) should also decrease. The HOMO-LUMO gap should become smaller.

22.7.

1.

The approximate calculation in Sec. 7 uses a trial wavefunction \(\phi(r) = 2\sqrt{\frac{\alpha^2}{\pi}} e^{-\alpha r}\). The kinetic and potential energy of one electron is \(T = \frac{\pi^2}{2}\) and \(V_{ext} = -\alpha Z\), respectively. The two-electron energy is \(V_{ee} = \frac{5\alpha}{8}\). The total energy is

\[
E = 2(\frac{\alpha^2}{2} - Z\alpha) + \frac{5\alpha}{8}
\]

(19)

Minimizing w.r.t. \(\alpha\) gives \(\alpha = Z_{eff} = Z - \frac{5}{16}\), a reduced effective nuclear charge due to screening.

The virial theorem for this system is \(2(2T) = -V_{ee} - 2V_{ext}\). This is satisfied for \(\alpha = 2 - \frac{5}{16}\).

The cusp condition \(\frac{dn}{dr} \bigg|_{r=0} = -2Zn(0)\) is also satisfied.

The ionization potential potential theorem is not satisfied: \(I = \frac{\alpha^2}{2} = 1.42\) is bad compared with \(I_{exact} = 0.88\).

2.

In a classical picture of electrostatics, the effective potential felt by an electron at a distance \(r'\) from the nucleus is \(V_{eff} = -Z_{eff}\frac{1}{r'}\) where the effective nuclear charge \(Z_{eff}(r')\) is the total charge enclosed by a sphere of radius \(r'\) (this is just Gauss’ law).

\[
Z_{eff}(r') = 2 - \int_0^{r'} |\phi(r)|^2 4\pi r'^2
\]

(20)

\[
= 2 - (1 + e^{-2\alpha r'}(-1 - 2\alpha r(1 + \alpha r)))
\]

(21)

The effective charge and potential are plotted in Figures 3 and 4, respectively (with \(\alpha = 2 - \frac{5}{16}\)). As \(r' \to 0\), \(Z_{eff}\) approaches 2 (e.g. no screening). When \(r' \to \infty\), the electron is fully screened and \(Z_{eff}\) becomes 1.

3.

Sum of one-electron energies is \(2(\frac{\alpha^2}{2} - Z\alpha)\), which leaves out the electron-electron repulsion (which is positive).
The energy of the two-electron ions is given by $E_2(Z) = aZ^2 + bZ + c$. The energy of the one-electron ion is given exactly by $E_1(Z) = -Z^2/2$. We solve for the smallest $Z_0$ such that $I(Z_0) = E_1(Z_0) - E_2(Z_0) = 0$. HF gives $a = -1$, $b = 0.623$, $c = -0.11$ and $Z_0 = 1.036$. The exact energies give $a = -1$, $b = 0.624$, $c = -0.15$ and $Z_0 = 0.918$. Figure 5 compares the two ionization potentials. What’s significant is that HF suggests that $H^-$, with $Z = 1$, is unstable since it has a negative ionization potential, while the exact result predicts otherwise. The difference between HF and the exact answer is the correlation energy, which therefore must be responsible for stabilizing $H^-$. 

FIG. 3 The effective nuclear charge an electron sees in He as a function of the distance from the nucleus.

FIG. 4 The effective potential felt by an electron in He.

FIG. 5 Comparison of our quadratic approximations to the ionization potential based on Hartree-Fock (red) and exact energies (black).