HW 7 Solutions

Problem #1   Schrödinger Equation for Helium

e^-

↑

$2+$ ⟶ e^-

$$\hat{H}\,\Psi(1,2) = \hat{E}\,\Psi(1,2)$$

$$\left\{ -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) + V(r_{12}) \right\}\Psi = E\Psi$$

$$\left\{ \frac{-\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\vec{r}_1|} + \frac{1}{|\vec{r}_2|}\right) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1| - |\vec{r}_2|} \right\}\Psi(1,2)$$

$$= E\Psi(1,2)$$

Problem #2   What does "Self - Consistent" mean?

using "independent electron" approximation, we get

$$\Psi(1,2) = \Psi(1)\,\Psi(2)$$

This makes it simpler to solve the Schrödinger.

given a guess Ψ_i, a self consistent field computes the potential ($\hat{V}_{coul}[\Psi_i]$, $\hat{V}_{ex}[\Psi_i]$, $\hat{V}_{corr}[\Psi_i]$), then it sets up a schrödinger equation and solves for Ψ_i, ε_i / E. New Ψ_i is compared to input. If sufficiently similar, stop. If not, create new Ψ_i until it is self consistent.

Problem #3   How many solutions are needed to describe electrons in the He atom?

$n = 1$

$\ell = 0$

$m\ell = 0$

Atomic #	n	ℓ	$m\ell$	m_s
2	1	0	0	$+\frac{1}{2}$
	1	0	0	$-\frac{1}{2}$

$1s$

$$\underline{\underline{2}}$$

new schrödinger equation with new Ψ_i and repeat until convergence.

Problem #4

$$\left\{ -\frac{\hbar^2}{2M_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}|} + V_{col}[\psi_i] + V_{ex}[\psi_i] + V_{corr}[\psi_i] \right\}\psi_i = E_i\,\psi_i$$

$-\frac{\hbar^2}{2M_e}\nabla^2 \longrightarrow$ kinetic energy $\quad > 0$

$-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}|} \longrightarrow$ attraction between nucleus and electron $\quad < 0$

$+ \; V_{col}[\psi_i] \longrightarrow e^- e^-$ repulsion average overall location $\quad > 0$

$+ \; V_{ex}[\psi_i] \longrightarrow$ account for QM indistinguichability of $e^- \quad < 0$
       and self interaction

$+ \; V_{corr}[\psi_i] \longrightarrow$ accounts for error in Coulomb, as electron
       will avoid one another $\qquad\qquad\qquad < 0$

HW7

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1 Chem 30324, Spring 2024, Homework 7

1.0.1 Sophisticated computer programs that solve the many-electron Schrödinger equation are now widely available and powerful tool for predicting the properties of atoms, molecules, solids, and interfaces. *Density functional theory* (DFT) is the most common set of approximations for the electron-electron interactions used today. In this problem you'll do a DFT calculation using the *Orca* program (https://www.its.hku.hk/services/research/hpc/software/orca).

1.0.2 Now, let's set up your calculation (you may do this with a partner or two if you choose):

1. Log into the Webmo server https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi using "guest" as your username and password.
2. Select New Job-Creat New Job.
3. Use the available tools to draw an atom on the screen.
4. Use the right arrow at the bottom to proceed to the Computational Engines.
5. Choose Orca
6. Select "Molecular Orbitals" for the Calculation type, "PBE" for theory, "def2-SVP" for the basis set, "0" for the charge, an appropriate value for the "Multiplicity", and check "Unrestricted."
7. Select the right arrow to run the calculation.
8. From the job manager window choose the completed calculation to view the results.
9. For fun, click on the Magnifying Glass icons to see the molecular orbitals in 3-D. You may have to play around with the Display Settings and Preferences to get good views.

1.0.3 5. Perform calculations across the first row of the periodic table (B, C, N, O, F, Ne). Make a table of energies of the occupied orbitals and identify them by their shell ($n = 1, 2, ...$) and subshell (s, p, d, ...).

See attached screenshot and Excel file for table. I have provided the alpha and beta spin energies for each orbital when applicable.

1.0.4 6. Contrast the energies of the 1s electrons across the series. Determine the wavelength of light necessary to remove each 1s electron. What range of the spectrum is this light in?

The energy of the 1s electrons decreases rapidly as you move across the series. Energy to ionize is roughly $-E_{1s}$. Dividing by hc gives the wavelengths provided below, which are in the x-ray range. For all calculations I will use the alpha spin energies.

For example, the the 1s energy for B is -6.6175 au. $1 au = 1 Hartree = 27.212$ eV, so converting to eV gives 180.06 eV. Using $hc \approx 1240 eV * nm$, we get that the wavelength is 6.89 nm, which is in the x-ray range.

1.0.5 7. Why, qualitatively, do the energies vary as they do?

As you move across the series, the nucleus of the atom is gaining more charge with each added proton. This added charge pulls on the 1s electron more tightly.

1.0.6 8. Compare the energies of the highest-energy (valence) electrons across the series. Determine the wavelength of light necessary to remove each valence electron. What range of the spectrum is this light in?

The energy of the valence electrons in the 2p orbitals are decreasing as you go across the series, but at a slower rate than the 1s electrons. Same strategy for calculations as with the 1s orbitals just using the . The wavelengths fall into the UV range from 100-300 nm.

1.0.7 9. Why, qualitatively, do the energies vary as they do?

As you move across the series, the nuclear charge is increasing with additional protons. The electrons in the same subshell are not effective at shielding each other, so as the effective charge increases the energy decreases.

		α	β
B	1s	-6.622	-6.613
	2s	-0.347	-0.311
	2p	-0.151	

		α	β
C	1s	-10.037	-9.993
	2s	-0.515	-0.421
	2p	-0.2172	

		α	β
N	1s	-14.0954	-14.04
	2s	-0.7034	-0.5354
	2p	-0.29199	

		α	β
O	1s	-18.8799	-18.83
	2s	-0.8839	-0.7532
	2p	-0.3782	-0.2515
		-0.3782	
		-0.2984	

		α	β
F	1s	-24.335	-24.307
	2s	-1.071	-0.998
	2p	-0.46475	-0.3444
		-0.373	

		α	
Ne	1s	-30.46	
	2s	-1.264	
	2p	-0.448	

	1s Energy	Energy (eV)	Wavelength (nm)
B	6.622	180.185	6.88183
C	10.037	273.107	4.54035
N	14.0954	383.536	3.23307
O	18.8799	513.722	2.41376
F	24.335	662.155	1.87267
Ne	30.46	828.817	1.49611

these are in the X-ray range

	2s Energy	Energy (eV)	Wavelength(nm)
B	0.151	4.10871	301.798
C	0.2172	5.91001	209.813
N	0.29199	7.94505	156.072
O	0.3782	10.2908	120.496
F	0.46475	12.6458	98.0559
Ne	0.448	12.1901	101.722

these are in the UV range