

The Hartree-Fock Applet

We would now like to show in more detail how one can use the Hartree-Fock applet at the web site of this book to obtain realistic atomic wave functions and to obtain average values of the variables used to describe the electrons and their interactions. As indicated in Section 5.5.1, the buttons along the lower edge of the applet web page allow one to select a particular atomic state and to specify how a Hartree-Fock calculation will be performed, while the tabs along the top of the page enable one to view the results of a calculation. We shall first illustrate how the buttons along the lower edge of the applet should be used by performing a number of Hartree-Fock calculations including one calculation that offers particular difficulties.

We begin by again performing a Hartree-Fock for the ground state of the lithium. One does this by first clicking on the Elements tab at the top of the web page and clicking on the *Li* atom. The web page shown in Fig. 5.8(a) appears on the screen with the ground state $1s^2 2s^2 S$ appearing in the lower left-hand corner of the page. The ground state of lithium has a filled $1s$ shell and a single electron in the $2s$ state. Since filled shells of electrons have zero values of both the total spin and orbital angular momentum, the spin and orbital angular momentum of the lithium atom are due to the single $2s$ electron which has $S = 1/2$ and $L = 0$. The state is denoted 2S in spectroscopic notation with the superscript 2 giving the value of $2S + 1$ and the letter S indicating that $L = 0$.

The Hartree-Fock applet easily be used to find the wave functions of the ground state of most atoms. To gain some understanding of the kinds of difficulties one can encounter for the excited states and how one can deal with the difficulties that arise, we shall now do a Hartree-Fock calculation for the excited $1s 2s^1 S$ state of the helium atom, which has a single electron in both the $1s$ and $2s$ shells. We first click on the element tab and click on the helium atom. The web page appears on the screen with the $1s^2^1 S$ state appearing in the lower left-hand corner. To remove an electron from the $1s$ shell of helium, we use the first set of up/down arrows on the bottom row of the applet to make the value of n of the electron 1 and then click on the $-e$ tab to remove an electron from the $1s$ shell. An electron can then be added to the $2s$ shell by changing the value of n of the electron to 2 and clicking the $+e$ tab. We can then see that the state of He given in the lower left hand corner is $1s^1 2s^1^1 S$.

To perform the Hartree-Fock calculation for the excited $1s^1 2s^1^1 S$ state of He, we now click the red arrow in the lower right-hand corner, and the applet then producing an error message saying that the Hartree-Fock calculation did not converge in 12 iterations. The source of the difficulty is that the $1s^1 2s^1^1 S$ state of He lies above the lowest $1s^2^1 S$ state. Even a small admixture of the $1s$ wave function of the $1s^2$ configuration into the $2s$ has a large perturbing effect upon the Hartree-Fock calculation for the $1s 2s$ configuration.

To overcome this difficulty, we first perform a Hartree-Fock calculation upon the $1s 2s^3 S$ state of He by using the arrow after $2S + 1$ on the bottom of the screen to raise the 1 to a 3. There is no $^3 S$ state of the $1s^2$ configuration to perturb the calculation for the $1s 2s^3 S$ state. Clicking the red arrow in the lower right-hand corner of the screen the applet runs successfully showing the

wave functions of the 1s and 2s wave functions on the screen. The average value of r for the 2s wave function is represented by a vertical blue line on the screen. The value of $\langle r \rangle$ is about 4.4. One can get a more accurate estimate for the average value of r of the 2s wave function by clicking the averages tab on the top of the screen. One finds that the average value of r for the 2s wave function for the $1s 2s^3S$ state of He is 4.37.

To perform a Hartree-Fock calculation for the $1s 2s^1S$ state of He, we first return to our original screen by clicking on the elements tab on the top of the screen and lower the value of $2S + 1$ on the bottom of the screen from 3 to 1 by using the arrow to the right of $2S + 1$. We are ready again to do a Hartree-Fock calculation for the $1s 2s^1S$ state of He. To ensure that this second calculation is successful, we click the button on lower right-hand corner of the screen showing two arrows forming a circular pattern. This will have the effect of using the Hartree-Fock wave functions for the $1s 2s^3S$ calculation as the initial approximation of the wave functions for the $1s 2s^1S$ calculation. We also click the next button to the left of the circular pattern with a vertical line meeting a lower horizontal line at right angles. This has the effect of forcing the 2s wave function to be orthogonal to the 1s wave function thereby stopping the mixing of the 1s wave function into the 2s wave function. It is this mixing which caused our previous Hartree-Fock calculation to fail. Clicking on the red arrow on the lower right-hand corner of the screen, the Hartree-Fock calculation then runs successfully producing the 1s and 2s wave functions on the screen. Clicking on the averages tab again, we see that the average value of r of the 2s wave function for the $1s 2s^1S$ state is 4.45. The 2s wave function in the excited triplet state is slightly more diffuse than the 2s wave function in the lower-lying singlet state.

The Hartree-Fock applet for the ground configuration of most atoms converges rapidly. While the Hartree-Fock method may converge slowly for excited states, one can usually obtain good results by running the applet for lower-lying states to produce good initial estimates of the wave functions and then requiring that excited orbitals be orthogonal to the orbitals with the same angular momentum in the ground configuration.

Additional information about a Hartree-Fock calculation can be found by clicking the tabs above the Hartree-Fock applet. The periodic table appears when one clicks the elements tab. Once one clicks on a particular element, the arrow in the lower right-hand corner will become red. A Hartree-Fock calculation will be performed when one clicks on the red arrow. Suppose one clicks on the elements tab, selects carbon, and clicks on the red arrow. The radial wave functions of the 1s, 2s, and 2p appear on the screen. One can obtain information about the average values of powers of r and about the potential and kinetic energy of the electrons by clicking on the averages tab. One can see that the average values of r and $1/r^3$ for the 2p orbital of carbon are 1.71 and 1.69, respectively. These average values, which are consistent with the values of $\langle r \rangle$ and $\langle 1/r^3 \rangle$ for the 2p given in Table 5.1, can also be obtained by clicking the other tab. On the first line of the web page which then appears, one uses the first arrow to raise the 1 to a 2, uses the second arrow to raise the s to a p, and then uses the third arrow to make k equal to 1. Clicking the arrow to the right, we get $\langle r \rangle = 1.714492$ atomic units. The average value of $F^2(2p, 2p)$ can be obtained using the second line of the applet. Using the arrows on the second line to make $k = 2$ and $nl = 2p$, we click on the arrow at the end of the second line to obtain $F^2(2p, 2p) = 0.2433018$ a.u. = $53398.409 \text{ cm}^{-1}$. This value is consistent with the value of $F^2(2p, 2p)$ for carbon given in Table 5.1. Similarly, using the third line of the applet, we find that the value of the spin-orbit constant $\zeta(2p)$ is equal to 31.942 cm^{-1} , which is again consistent with the value given in Table 5.1.