

Although these calculations do show that we can obtain essentially exact energies by using the variational method with r_{12} in the trial function explicitly, these calculations are quite difficult computationally and do not readily lend themselves to large atoms and molecules. Furthermore, we have abandoned the orbital concept altogether. The Hartree-Fock orbital concept has been of great use to chemists, so the scheme nowadays is to find the Hartree-Fock orbitals mentioned above and correct them by some method such as perturbation theory. It is instructive to outline the Hartree-Fock procedure for helium because the equations are fairly simple for this two-electron case and provide a nice physical interpretation.

8-3. Hartree-Fock Equations Are Solved by the Self-Consistent Field Method

The starting point of the Hartree-Fock procedure for helium is to write the two-electron wave function as a product of orbitals, as in Equation 8.15:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \quad (8.17)$$

The two functions on the right side of Equation 8.17 are the same because we are assuming that both electrons are in the same orbital, in accord with the Pauli Exclusion Principle. According to Equation 8.17, the probability distribution of electron 2 is $\phi^*(\mathbf{r}_2)\phi(\mathbf{r}_2)d\mathbf{r}_2$. We can also interpret this probability distribution classically as a charge density, and so we can say that the potential energy that electron 1 experiences at the point \mathbf{r}_1 due to electron 2 is (in atomic units)

$$V_{\text{eff}}^1(\mathbf{r}_1) = \int \frac{\phi^*(\mathbf{r}_2)\phi(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \quad (8.18)$$

where the superscript "eff" emphasizes that $V_{\text{eff}}^1(\mathbf{r}_1)$ is an effective, or average, potential. We now define an effective one-electron Hamiltonian operator by

$$H_{\text{eff}}^1(\mathbf{r}_1) = -\frac{1}{2}\Delta_{\mathbf{r}_1}^2 - \frac{r_1}{2} + V_{\text{eff}}^1(\mathbf{r}_1) \quad (8.19)$$

The Schrödinger equation corresponding to this effective Hamiltonian operator is

$$H_{\text{eff}}^1(\mathbf{r}_1)\phi(\mathbf{r}_1) = \epsilon_1\phi(\mathbf{r}_1) \quad (8.20)$$

There is a similar equation for $\phi(\mathbf{r}_2)$, but because $\phi(\mathbf{r}_1)$ and $\phi(\mathbf{r}_2)$ have the same functional form, we need to consider only one equation like Equation 8.20. Equation 8.20 is the *Hartree-Fock equation* for a helium atom, and its solution gives the best orbital wave function for helium. Note that $H_{\text{eff}}^1(\mathbf{r}_1)$ depends upon $\phi(\mathbf{r}_2)$ through Equation 8.18. Thus, we must know the solution to Equation 8.20 before we even know the operator. The method of solving an equation like Equation 8.20 is by a scheme called the *self-consistent field method*, which can be implemented very easily on a computer.

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