ATOMIC WAVEFUNCTIONS: SYMMETRIZATION

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.8.

So far, we've looked at identical particles only in the non-interacting case. In real life, of course, most particles interact with each other, so the Schrödinger equation must take this into account. For an atom with Z protons and Z electrons, each electron experiences an electric interaction with the nucleus, and with all the other electrons. The Schrödinger equation in this case is therefore

$$(0.1) \qquad H\psi = E\psi$$

where

$$(0.2) \qquad H = \sum_{j=1}^{Z}\left[-\frac{\hbar^2}{2m}\nabla_j^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_j}\right] + \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{j\neq k}\frac{e^2}{\left|\mathbf{r}_j - \mathbf{r}_k\right|}$$

The first term in the first sum is the kinetic energy of the electrons (we're assuming the atom as a whole is at rest, so there is no contribution from the kinetic energy of the nucleus), the second term gives the interaction between the electrons and the nucleus, and the last sum gives the electron-electron interactions.

Needless to say, solving this equation is very difficult and in fact, there is no known exact solution except in the case of hydrogen, where $Z = 1$ and the last term vanishes.

If we *could* find a solution, however, we'd need to form a completely anti-symmetric function from it, since electrons are fermions. The general solution would have the form

$$(0.3) \qquad \psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_Z)$$

Since the hamiltonian is completely symmetric with respect to the Z vectors $\mathbf{r}_i$, any permutation of the vectors in the solution is also a solution, so any linear combination of solutions is also a solution, and will have the same energy.

Since the anti-symmetry results from interchanging position vectors, we can apply the same process as that used to find anti-symmetric wave functions from stationary states. This time, however, we apply the anti-symmetrization to the order of the vectors in the argument list, rather than to individual stationary states. Thus, we'd get

$$(0.4) \qquad \psi_f = A \left[\sum_{even} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_Z) - \sum_{odd} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_Z) \right]$$

where the first sum is over all even permutations of the vectors and the second is over all odd permutations. The constant A is determined by normalization.

In the case of bosons we just replace the minus sign by a plus sign, which results in a sum over all permutations

$$(0.5) \qquad \psi_b = A \sum_{all} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_Z)$$

This would, of course, not apply to the hamiltonian above, since electrons are not bosons, but if we did have a hamiltonian that applied to a collection of bosons, we could use the same procedure to generate a symmetric wave function.