# 38

# The Two-Electron Atom

The indistinguishability of identical particles in quantum mechanics plays a very important role. In macroscopic, classical physics we can tag our particles (by painting infinitesimally small labels on them!) so we can distinguish those labelled, 1, 2, etc., even though they have exactly the same mass, internal constitution, etc. The impossibility of such a tagging procedure plays a very fundamental role in quantum mechanics.

Consider one of the simplest systems with identical particles, the two-electron He atom, with Hamiltonian

$$H = \frac{\vec{p}_1^{\,2}}{2\mu} + V(r_1) + \frac{\vec{p}_2^{\,2}}{2\mu} + V(r_2) + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + H_{\text{f.s.}}(\vec{r}_1, \vec{p}_1, \vec{\sigma}_1; \vec{r}_2, \vec{p}_2, \vec{\sigma}_2), \quad (1)$$

where only the last term is dependent on the spins of the two electrons and depends on these through their Pauli $\vec{\sigma}$ vectors. This fine structure term will include one-body spin-orbit and Thomas terms, two-body spin-magnetic moment-spin-magnetic moment interactions, and so on, and can be treated as truly small perturbations on the zeroth-order terms including the Coulomb repulsion term, $e^2/r_{12}$. Even with all fine structure terms, however, the Hamiltonian has a strictly valid symmetry. It is invariant under the interchange of the particle indices, 1 and 2.

$$\begin{aligned} H(\vec{r}_1, \vec{p}_1, \vec{\sigma}_1; \vec{r}_2, \vec{p}_2, \vec{\sigma}_2)) &= H(\vec{r}_2, \vec{p}_2, \vec{\sigma}_2; \vec{r}_1, \vec{p}_1, \vec{\sigma}_1) \\ &= P_{12} H(\vec{r}_1, \vec{p}_1, \vec{\sigma}_1; \vec{r}_2, \vec{p}_2, \vec{\sigma}_2) P_{12}^{-1}, \end{aligned} \quad (2)$$

where the operator $P_{12} \equiv P_{12}^{-1}$ exchanges the indices 1 and 2 on all electron variables. $P_{12}$ commutes with the Hamiltonian, $H$. The eigenfunctions of the operator

$P_{12}$ are the symmetric and antisymmetric functions

$$\psi^{(s)} = \frac{1}{\sqrt{2}}\big[\psi(\vec{r}_1, \vec{\sigma}_1; \vec{r}_2, \vec{\sigma}_2) + \psi(\vec{r}_2, \vec{\sigma}_2; \vec{r}_1, \vec{\sigma}_1)\big],$$
$$\psi^{(a)} = \frac{1}{\sqrt{2}}\big[\psi(\vec{r}_1, \vec{\sigma}_1; \vec{r}_2, \vec{\sigma}_2) - \psi(\vec{r}_2, \vec{\sigma}_2; \vec{r}_1, \vec{\sigma}_1)\big], \tag{3}$$

with eigenvalues $+1$ and $-1$, respectively, for the operator $P_{12}$. Thus. it seems that every energy level of the two-electron $H$ must be two-fold degenerate to all orders in perturbation theory, because the energy eigenfunctions can be either symmetric or antisymmetric. Even more, any linear combination of the symmetric and antisymmetric functions will have the same energy. Thus,

$$\Psi = c_s\psi^{(s)} + c_a\psi^{(a)}, \qquad \text{with} \qquad |c_s|^2 + |c_a|^2 = 1, \tag{4}$$

is an equally acceptable energy eigenfunction of our $H$. This function, however, leads to a tremendous dilemma. For this last $\Psi$, with arbitrary $c_s$ and $c_a$, the probability one electron is at position $\vec{r}_0$, with spin alignment $\vec{\sigma}_0$, and the other electron is at position $\vec{r}_0'$, with spin alignment $\vec{\sigma}_0'$, is given by

$$\begin{aligned} P(\vec{r}_0, \vec{\sigma}_0; \vec{r}_0', \vec{\sigma}_0') &= |\Psi(\vec{r}_0, \vec{\sigma}_0; \vec{r}_0', \vec{\sigma}_0')|^2 + |\Psi(\vec{r}_0', \vec{\sigma}_0'; \vec{r}_0, \vec{\sigma}_0)|^2 \\ &= |c_s\psi^{(s)} + c_a\psi^{(a)}|^2 + |c_s\psi^{(s)} - c_a\psi^{(a)}|^2 \\ &= 2(|c_s|^2|\psi^{(s)}|^2 + |c_a|^2|\psi^{(a)}|^2). \end{aligned} \tag{5}$$

We must add the probability the electron we have labeled 1 is at $\vec{r}_0$ with spin alignment given by $\vec{\sigma}_0$, and electron 2 is at the primed position with primed spin alignment, to the probability the electron we have labeled 2 is at position $\vec{r}_0$ with spin alignment given by $\vec{\sigma}_0$, because we cannot distinguish electrons 1 and 2. Also, this probability, a physically measurable quantity, seems to be dependent on $c_s$ and $c_a$. Because $c_s$ can vary between 0 and 1, it seems this physically measurable quantity has an essentially arbitrary predicted value. Consider, in particular, the special case in which both electrons are situated at the same position, $\vec{r}_0$, and both have the same spin alignment given by $\vec{\sigma}_0$. In this case $\psi^{(a)} = 0$, so in this case this probability would be $2|c_s|^2|\psi^{(s)}|^2$. Because $c_s$ can vary between 0 and 1, this probability could seemingly be anything between 0 and a maximum of $2|\psi^{(s)}|^2$. The way out of this seeming dilemma is furnished by nature herself! An additional property of nature exists, first discovered empirically. The states of a system of $n$ identical particles are either all totally symmetric or all totally antisymmetric.

The totally symmetric states are symmetric under any pair exchange and hence under any number of pair exchanges or any permutation of the $n$ particle indices. This symmetry holds for systems of identical particles with integer spins; that is, $s = 0, 1, 2, \cdots$. Such particles are known as Bose–Einstein particles or as bosons.

The totally antisymmetric states change sign under any pair exchange and, hence, any odd permutation of the particle indices involving an odd number of pair exchanges, while they do not change sign under even permutations of the particle indices, involving an even number of pair exchanges. This case applies to systems of identical particles with $\frac{1}{2}$-integral spin, $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$. Such particles are known as Fermi–Dirac particles or as fermions.

Because electrons have $s = \frac{1}{2}$, they are fermions and belong to the antisymmetric case. The antisymmetry, however, applies to the total wave function. A two-electron system could have a two-particle orbital wave function symmetric under the pair exchange operator applied to orbital states, provided it is multiplied by an antisymmetric two-particle spin function, or vice versa. Because our Hamiltonian is spin-independent in first approximation (where we can neglect spin-orbit and spin magnetic-moment-spin magnetic moment interactions), we would expect a product of purely orbital and purely spin functions to be a good approximation. Let us look at the two-particle spin function first. Let us, in particular, couple the two single-particle spins $s$ to resultant two-particle spin, $S$. Later, we shall specialize to the electron case with $s = \frac{1}{2}$. For the moment, let $s$ be arbitrary.

$$\psi(\vec{s}_1, \vec{s}_2)^S_{M_S} = \sum_{m_{s_a}, m_{s_b}} \psi_{m_{s_a}}(\vec{s}_1)\psi_{m_{s_b}}(\vec{s}_2)\langle s m_{s_a} s m_{s_b} | S M_S\rangle. \tag{6}$$

Now, act on this $\psi$ with the operator $P^s_{12}$, where the superscript $s$ indicates we permute indices only on spin functions

$$P^s_{12}\psi(\vec{s}_1, \vec{s}_2)^S_{M_S} = \sum_{m_{s_a}, m_{s_b}} \psi_{m_{s_a}}(\vec{s}_2)\psi_{m_{s_b}}(\vec{s}_1)\langle s m_{s_a} s m_{s_b} | S M_S\rangle. \tag{7}$$

Now, in the sum over the indices, $m_{s_a}, m_{s_b}$, let us rename the dummy indices, $m_{s_a} \leftrightarrow m_{s_b}$, and let us then rewrite the product of the two single-particle spin functions in reverse order, to obtain

$$P^s_{12}\psi(\vec{s}_1, \vec{s}_2)^S_{M_S} = \sum_{m_{s_a}, m_{s_b}} \psi_{m_{s_a}}(\vec{s}_1)\psi_{m_{s_b}}(\vec{s}_2)\langle s m_{s_b} s m_{s_a} | S M_S\rangle. \tag{8}$$

Next, we make use of the symmetry property of the Clebsch–Gordan coefficient

$$\langle s m_{s_b} s m_{s_a} | S M_S\rangle = (-1)^{2s-S}\langle s m_{s_a} s m_{s_b} | S M_S\rangle \tag{9}$$

to obtain

$$P^s_{12}\psi(\vec{s}_1, \vec{s}_2)^S_{M_S} = (-1)^{2s-S}\psi(\vec{s}_1, \vec{s}_2)^S_{M_S}. \tag{10}$$

Thus, with $s = \frac{1}{2}$-integer, so $2s$ = odd integer, two-particle spin functions, with $S = 0, 2, \cdots$, even integer, are antisymmetric, whereas two-particle spin functions, with $S = 1, 3, \cdots$, odd integer, are symmetric. For the special case of electrons, with $s = \frac{1}{2}$, the two-particle state with $S = 0$ is antisymmetric, whereas the two-particle states with $S = 1$ are symmetric. The antisymmetric two-particle spin states, with $S = 0$, must now be matched with a symmetric two-particle orbital state; similarly, the symmetric two-particle spin states, with $S = 1$, must be matched with antisymmetric two-particle orbital states. For two-electron states with $n_a l_a \neq n_b l_b$, we can always construct both a symmetric and an antisymmetric two-particle orbital state of good two-particle orbital angular momentum, $L$, $M_L$

$$\psi_{n_a l_a; n_b l_b}(\vec{r}_1, \vec{r}_2)^L_{M_L} = \sum_{m_a, m_b} \Big[\psi_{n_a l_a m_a}(\vec{r}_1)\psi_{n_b l_b m_b}(\vec{r}_2) \pm \psi_{n_b l_b m_b}(\vec{r}_1)\psi_{n_a l_a m_a}(\vec{r}_2)\Big]\langle l_a m_a l_b m_b | L M_L\rangle$$

$$= \sum_{m_a, m_b} \Big[ \psi_{n_a l_a m_a}(\vec{r}_1)\psi_{n_b l_b m_b}(\vec{r}_2)\langle l_a m_a l_b m_b | L M_L\rangle$$

$$\pm \psi_{n_b l_b m_b}(\vec{r}_1)\psi_{n_a l_a m_a}(\vec{r}_2)(-1)^{l_a+l_b-L}\langle l_b m_b l_a m_a | L M_L\rangle \Big], \qquad (11)$$

where the upper sign refers to the orbitally symmetric and the lower sign to the orbitally antisymmetric two-particle functions. In the special case, when $n_a = n_b = n$ and $l_a = l_b = l$, we can rename the indices $m_a \leftrightarrow m_b$ in the second term of this equation because they are dummy summation indices. With $n_a = n_b = n$, and $l_a = l_b = l$, therefore, the symmetric and antisymmetric two-particle orbital states of good orbital angular momentum $L$, $M_L$ become

$$\psi_{nl;nl}(\vec{r}_1, \vec{r}_2)^L_{M_L} = \sum_{m_a m_b} \psi_{nlm_a}(\vec{r}_1)\psi_{nlm_b}(\vec{r}_2)\Big[1 \pm (-1)^{2l-L}\Big]\langle l m_a l m_b | L M_L\rangle. \quad (12)$$

Because $2l$ = even integer, in this case, symmetric two-particle states survive only for states with even L [upper sign in eq. (12)], whereas antisymmetric two-particle states survive only for states with odd L [lower sign in eq. (12)]. Thus, in two-electron configurations with $n_a l_a = n_b l_b$, the only allowed states must have either $S = 0$ and $L$ = even integer, or $S = 1$ and $L$ = odd integer. For a two-electron configuration of type $(np)^2$ in a two-valence electron atom, the only possible energy states are

$$^1S_0, \qquad ^1D_2, \qquad \text{and} \qquad ^3P_{0,1,2},$$

in standard spectroscopic notation, where $S$ is identified through a left superscript $(2S + 1)$, $L$ is identified by the spectroscopic letter, a capital letter because the state is not a one-electron state, and the possible $J$ values are given by a right subscript. In the He atom, the ground state with $n_a l_a = n_b l_b = 10$, i.e., with ground-state configuration $(1s)^2$, must be a pure singlet state with $L = 0$, $S = 0$, i.e., a $^1S_0$ state. Excited states with configurations such as $(1s, 2s)$ or $(1s, 2p)$ have both a singlet and a triplet component, with $L = 0$ and $L = 1$, respectively, as shown in Fig. 38.1. Because only the small fine structure terms in our Hamiltonian have a spin dependence, the singlet and triplet states are almost unconnected. In addition, electromagnetic transitions between singlet and triplet states are forbidden in zeroth (electric dipole approximation), because the transition operator is spin-independent. Thus, the singlet, $S = 0$ state atoms, the so-called para-helium atoms, and the triplet, $S = 1$ state atoms, the so-called ortho-helium atoms, essentially form a mixture of two gases; transitions from singlet to triplet states being extremely rare. Finally, configurations such as $(2s)^2$ or $(2p)^2$ are not included in Fig. 38.1 because they can be expected to lie above the first ionization threshhold.

## A Perturbation Theory for a Two-Electron Atom

To get a very rough idea of the energy spectrum for He (or once ionized Li, twice ionized Be, etc), let us neglect all spin-dependent fine structure terms in the Hamiltonian of eq. (1) and, even further, try to consider the Coulomb repulsion

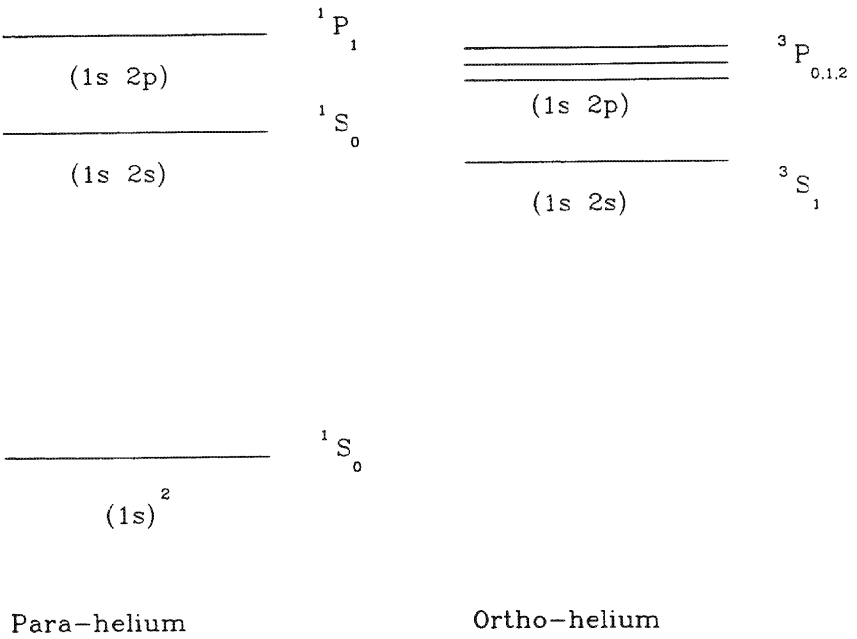


FIGURE 38.1. He atom spectrum.

term, $e^2/r_{12}$, as a first order perturbation. In eq. (1), the variables $r_1$, $r_2$ are the physical coordinates. Let us again introduce dimensionless $r_1$ and $r_2$. Because we will now find it useful to separate the $Z$ dependence of the various terms, let us make the substitutions

$$\vec{r}_{\text{phys.};i} = \frac{1}{Z}\frac{\hbar^2}{\mu e^2}\vec{r}_i, \qquad H_{\text{phys.}} = \frac{\mu e^4}{\hbar^2}H, \tag{13}$$

where all quantities without the subscript, phys., such as $\vec{r}_1$ and $\vec{r}_2$ are now dimensionless quantities, i.e., physical quantities given in atomic units. Then,

$$H = H^{(0)} + H^{(1)} = Z^2\Big(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{1}{r_2}\Big) + Z\frac{1}{r_{12}}. \tag{14}$$

With energies given in units of $\mu e^4/\hbar^2$, we get the dimensionless zeroth-order energy

$$E^{(0)} = -Z^2\Big(\frac{1}{2n_a^2} + \frac{1}{2n_b^2}\Big), \tag{15}$$

and the first-order corrections (albeit very rough corrections!) to this energy would be given by the diagonal matrix elements of $H^{(1)}$. If, for the moment, we use the shorthand notation $a \equiv n_a l_a m_a$ and $b \equiv n_b l_b m_b$, the zeroth-order state vectors for

the two-electron system are

$$\frac{1}{\sqrt{2}}\big(|ab\rangle + |ba\rangle\big)|S = 0, M_S = 0\rangle,$$
$$\frac{1}{\sqrt{2}}\big(|ab\rangle - |ba\rangle\big)|S = 1, M_S\rangle, \tag{16}$$

where the notation assumes the orbital quantum number, $a$ or $b$, which appears first in the ket, refers to the particle with label 1 and that which appears second refers to particle with label 2. Because our $H^{(1)} = Z/r_{12}$ is spin-independent, no off-diagonal terms connect $S = 0$ states to $S = 1$ states. The spin states simply furnish a spin-space orthonormality integral. No spin dependence of the matrix elements exists. Therefore,

$$E^{(1)} = \frac{1}{2}\left(\Big[\langle ab|H^{(1)}|ab\rangle + \langle ba|H^{(1)}|ba\rangle\Big] \pm \Big[\langle ab|H^{(1)}|ba\rangle + \langle ba|H^{(1)}|ab\rangle\Big]\right). \tag{17}$$

Now, use

$$\begin{aligned}\langle ba|H^{(1)}|ba\rangle &= \langle ba|P_{12}^{-1}P_{12}H^{(1)}P_{12}^{-1}P_{12}|ba\rangle \\ &= \langle ab|P_{12}H^{(1)}P_{12}^{-1}|ab\rangle = \langle ab|H^{(1)}|ab\rangle,\end{aligned} \tag{18}$$

with a similar relation for $\langle ba|H^{(1)}|ab\rangle$, so

$$E^{(1)} = \langle ab|H^{(1)}|ab\rangle \pm \langle ab|H^{(1)}|ba\rangle = D_{ab} \pm X_{ab}, \tag{19}$$

where $D_{ab}$ stands for the direct integral in which the order of the quantum numbers $ab$ is the same in both bra and ket, whereas $X_{ab}$ stands for the exchange integral in which the order of the quantum numbers $ab$ is exchanged in the ket relative to the order in the bra. The upper sign (+) refers to the singlet or $S = 0$ states, whereas the lower sign (-) refers to the triplet $S = 1$ states. Because our $H^{(1)} = +Z/r_{12}$ is a positive (repulsive) interaction term, we can expect both $D_{ab}$ and $X_{ab}$ to be positive numbers. Thus, we would expect the triplet states to lie somewhat below the singlet states, as shown in Fig. 38.1. This is a special case of Hund's rule. In a many-electron atom, we would expect the state with the largest possible number of electron pairs coupled to spin $S = 1$ to lie lowest in energy. Thus, the lowest state should be the state with highest possible total spin $S$.

Finally, our final energies are spin-dependent, even though our Hamiltonian was spin-independent, the spin dependence coming from the symmetry of the two-electron orbital functions. The antisymmetric two-particle orbital functions have a smaller probability of bringing the two electrons close together. Hence, in these states, the Coulomb repulsion term between the two electrons is less effective. The resultant apparent spin-dependence of the Hamiltonian could be taken into account by introducing an effective spin-dependent Hamiltonian,

$$H_{ab}^{(1)} = D_{ab} - X_{ab}\frac{(1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2)}{2}, \tag{20}$$

where we have used

$$P_{12}^{\sigma} = \tfrac{1}{2}(1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2) = \tfrac{1}{2}(1 + 4\vec{s}_1 \cdot \vec{s}_2) = \tfrac{1}{2}(1 + 2[S(S+1) - \tfrac{3}{4} - \tfrac{3}{4}]), \tag{21}$$

which has eigenvalue $+1$ for an $S = 1$, or spin-symmetric state and eigenvalue $-1$ for an $S = 0$ or spin-antisymmetric state.

To actually carry out the direct and exchange integrals, we will expand $1/r_{12}$ in spherical harmonics

$$\begin{aligned}\frac{1}{|\vec{r}_1 - \vec{r}_2|} &= \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}}} \\ &= \sum_{k=0}^{\infty} \frac{r_2^k}{r_1^{k+1}} P_k(\cos\theta_{12}), \qquad \text{for} \quad r_2 < r_1, \\ &= \sum_{k=0}^{\infty} \frac{r_1^k}{r_2^{k+1}} P_k(\cos\theta_{12}), \qquad \text{for} \quad r_1 < r_2. \end{aligned} \tag{22}$$

We shall further use the addition theorem for spherical harmonics

$$P_k(\cos\theta_{12}) = \frac{4\pi}{(2k+1)} \sum_q Y_{kq}^*(\theta_1, \phi_1) Y_{kq}(\theta_2, \phi_2). \tag{23}$$

The direct term, $D_{ab}$, is made up of terms of the form

$$\begin{aligned} D_{ab} = Z \sum_{k=0}^{\infty} \sum_q \frac{4\pi}{(2k+1)} &\int_0^{\infty} dr_1 r_1^2 R_{n_a l_a}^2(r_1) \\ &\times \left[ \int_0^{r_1} dr_2 r_2^2 \frac{r_2^k}{r_1^{k+1}} R_{n_b l_b}^2(r_2) + \int_{r_1}^{\infty} dr_2 r_2^2 \frac{r_1^k}{r_2^{k+1}} R_{n_b l_b}^2(r_2) \right] \\ &\times \int\int d\Omega_1 Y_{l_a(m_a - q)}^*(\theta_1, \phi_1) Y_{kq}^*(\theta_1, \phi_1) Y_{l_a m_a}(\theta_1 \phi_1) \\ &\times \int\int d\Omega_2 Y_{l_b(m_b + q)}^*(\theta_2, \phi_2) Y_{kq}(\theta_2, \phi_2) Y_{l_b m_b}(\theta_2, \phi_2), \end{aligned} \tag{24}$$

weighted by the appropriate Clebsch–Gordan coefficients for the coupling $[l_a \times l_b]LM$. The angular integrals will in general greatly restrict the number of terms in the $k$ sum. For the low-lying states of He, in particular, with one of the $n_a l_a$ or $n_b l_b = 10$, in general, just a single $k$ term will exist. For the He ground state, for example, with $n_a l_a = n_b l_b = 10$, the angular integrals give

$$\int\int d\Omega Y_{00}^*(\theta, \phi) Y_{kq}(\theta, \phi) Y_{00}(\theta, \phi) = \delta_{k0}\delta_{q0} \frac{1}{\sqrt{4\pi}}, \tag{25}$$

so the energy, $E^{(1)}$, which is here given by the direct integral, gives

$$E^{(1)} = Z \int_0^{\infty} dr_1 r_1^2 R_{10}^2(r_1) \left[ \int_0^{r_1} dr_2 r_2^2 \frac{1}{r_1} R_{10}^2(r_2) + \int_{r_1}^{\infty} dr_2 r_2^2 \frac{1}{r_2} R_{10}^2(r_2) \right]. \tag{26}$$

With $R_{10}(r) = 2e^{-r}$, and

$$\int_0^{r_1} dr_2 4r_2^2 e^{-2r_2} = \left[ e^{-2r} \left( -2r^2 - 2r - 1 \right) \right]_0^{r_1}, \tag{27}$$

and

$$\int_{r_1}^{\infty} dr_2 4r_2 e^{-2r_2} = -\left[e^{-2r}\left(2r+1\right)\right]_{r_1}^{\infty}, \tag{28}$$

we get

$$\begin{aligned} E^{(1)} &= Z\left(4\int_0^{\infty} dr_1 r_1 e^{-2r_1} - 4\int_0^{\infty} dr_1 (r_1^2 + r_1) e^{-4r_1}\right) \\ &= Z(1! - \frac{2!}{16} - \frac{1!}{4}) = \frac{5}{8}Z. \end{aligned} \tag{29}$$

Thus, including this "first-order" correction term, the He atom ground-state energy would be (in atomic units $\mu e^4/\hbar^2$)

$$E = E^{(0)} + E^{(1)} = -Z^2 + \frac{5}{8}Z, \tag{30}$$

with $Z = 2, 3, \cdots$ for He, once ionized Li, $\cdots$. For He, therefore, we get

$$E \approx -4 + \frac{5}{4} = -2.75. \tag{31}$$

This result compares with the experimental value of $-2.90351$. Considering the highly approximate nature of our calculation, this is not a bad result, but clearly improvements are necessary. This need for improvement will lead us to our final perturbation technique, the variational method. Before we discuss this perturbation technique, we need to make a few remarks about $n$ identical-particle systems, with $n > 2$.