Phys 130B   QM II

Identical Particles

1   Two-Particle Systems

Suppose we have two particles that interact under a mutual force with potential energy $\widetilde{V}(\mathbf{x}_1 - \mathbf{x}_2)$, and are also moving in an external potential $V(\mathbf{x}_i)$. Then the Hamiltonian is $H = T_1 + T_2 + \widetilde{V} + V(\mathbf{x}_1) + V(\mathbf{x}_2)$ so the time-dependent Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + \widetilde{V}(\mathbf{x}_1 - \mathbf{x}_2) + V(\mathbf{x}_2) + V(\mathbf{x}_2) \right] \Psi(\mathbf{x}_1, \mathbf{x}_2, t)$$
$$= i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x}_1, \mathbf{x}_2, t) \quad (1)$$

where $\boldsymbol{\nabla}_i^2$ refers to the laplacian with respect to the coordinates of particle i.

To solve this equation, we first separate time and spatial variables in the usual manner by writing

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, t) = \psi(\mathbf{x}_1, \mathbf{x}_2)T(t)$$

and substituting this into (1). Dividing both sides by ψT yields

$$\frac{1}{\psi}\left[-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + \widetilde{V}(\mathbf{x}_1 - \mathbf{x}_2) + V(\mathbf{x}_2) + V(\mathbf{x}_2) \right] \psi = \frac{i\hbar}{T}\frac{\partial T}{\partial t}\,.$$

Since the left side is a function of spatial variables only and the right side is a function of time only, both sides must be equal to a constant which we call E. Then the time equation has the solution (up to normalization)

$$T(t) = e^{-iEt/\hbar} \tag{2a}$$

and the spatial equation becomes

$$\left[-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + \widetilde{V}(\mathbf{x}_1 - \mathbf{x}_2) + V(\mathbf{x}_2) + V(\mathbf{x}_2) \right] \psi(\mathbf{x}_1, \mathbf{x}_2) = E\psi(\mathbf{x}_1, \mathbf{x}_2)$$
$$\tag{2b}$$

If the solutions to (2b) are E_n and $\psi_n(\mathbf{x}_1, \mathbf{x}_2)$, then the general solution to (1) is of the form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, t) = \sum_n c_n\psi_n(\mathbf{x}_1, \mathbf{x}_2)e^{-iE_nt/\hbar}\,.$$

Now we interpret $|\Psi(\mathbf{x}_1, \mathbf{x}_2, t)|^2$ as the probability density for particle i to be in the volume $d^3\mathbf{x_i}$, and the constants c_n are chosen so as to normalize the wave function to

$$\int |\Psi(\mathbf{x}_1, \mathbf{x}_2, t)|^2 \, d^3\mathbf{x}_1 \, d^3\mathbf{x}_2 = 1\,.$$

Let us now specialize to the case where the external potentials vanish. In this case, (2b) becomes

$$\left[-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + V(\mathbf{x}_1 - \mathbf{x}_2) \right] \psi(\mathbf{x}_1, \mathbf{x}_2) = E\psi(\mathbf{x}_1, \mathbf{x}_2) \tag{3}$$

where we now drop the tilde on $\widetilde{V}$. The presence of the term $\mathbf{x}_1 - \mathbf{x}_2$ suggests that we change variables from $\mathbf{x}_1$ and $\mathbf{x}_2$ to

$$\mathbf{r} = \mathbf{x}_1 - \mathbf{x}_2 \tag{4a}$$

$$\mathbf{R} = \alpha\mathbf{x}_1 + \beta\mathbf{x}_2 \, . \tag{4b}$$

We will see that these turn out to be the usual center-of-mass coordinates.

Using the chain rule, we have

$$\frac{\partial}{\partial x_{1i}} = \frac{\partial r_j}{\partial x_{1i}}\frac{\partial}{\partial r_j} + \frac{\partial R_j}{\partial x_{1i}}\frac{\partial}{\partial R_j} = \frac{\partial}{\partial r_i} + \alpha\frac{\partial}{\partial R_i}$$

$$\frac{\partial}{\partial x_{2i}} = -\frac{\partial}{\partial r_i} + \beta\frac{\partial}{\partial R_i}$$

so that

$$\boldsymbol{\nabla}_1^2 = (\partial_{r_i} + \alpha\partial_{R_i})(\partial_{r_i} + \alpha\partial_{R_i}) = \boldsymbol{\nabla}_r^2 + 2\alpha\boldsymbol{\nabla}_r \cdot \boldsymbol{\nabla}_R + \alpha^2\boldsymbol{\nabla}_R^2$$

$$\boldsymbol{\nabla}_2^2 = (-\partial_{r_i} + \beta\partial_{R_i})(-\partial_{r_i} + \beta\partial_{R_i}) = \boldsymbol{\nabla}_r^2 - 2\beta\boldsymbol{\nabla}_r \cdot \boldsymbol{\nabla}_R + \beta^2\boldsymbol{\nabla}_R^2$$

(where $\partial_{r_i} = \partial/\partial r_i$ etc). Therefore

$$\frac{1}{m_1}\boldsymbol{\nabla}_1^2 + \frac{1}{m_2}\boldsymbol{\nabla}_2^2 = \frac{1}{\mu}\boldsymbol{\nabla}_r^2 + 2\left(\frac{\alpha}{m_1} - \frac{\beta}{m_2}\right)\boldsymbol{\nabla}_r \cdot \boldsymbol{\nabla}_R + \left(\frac{\alpha^2}{m_1} + \frac{\beta^2}{m_2}\right)\boldsymbol{\nabla}_R^2$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

is called the **reduced mass**. We can eliminate the cross-term by choosing

$$\beta = \frac{m_2}{m_1}\alpha \tag{5}$$

which results in

$$\frac{1}{m_1}\boldsymbol{\nabla}_1^2 + \frac{1}{m_2}\boldsymbol{\nabla}_2^2 = \frac{1}{\mu}\boldsymbol{\nabla}_r^2 + M\frac{\alpha^2}{m_1^2}\boldsymbol{\nabla}_R^2$$

with $M = m_1 + m_2$.

Our choice of alpha is still arbitrary, and it is most convenient to choose it so that

$$\int d^3\mathbf{x}_1 \, d^3\mathbf{x}_2 = \int d^3\mathbf{r} \, d^3\mathbf{R}$$

2

which means the Jacobian of the transformation must be unity. In other words, letting x_{ij} be the jth component of $\mathbf{x}_i$ we have

$$
\begin{bmatrix}
\partial r_1/\partial x_{11} & \partial r_1/\partial x_{12} & \partial r_1/\partial x_{13} & \partial r_1/\partial x_{21} & \partial r_1/\partial x_{22} & \partial r_1/\partial x_{23} \\
\partial r_2/\partial x_{11} & \partial r_2/\partial x_{12} & \partial r_2/\partial x_{13} & \partial r_2/\partial x_{21} & \partial r_2/\partial x_{22} & \partial r_2/\partial x_{23} \\
\partial r_3/\partial x_{11} & \partial r_3/\partial x_{12} & \partial r_3/\partial x_{13} & \partial r_3/\partial x_{21} & \partial r_3/\partial x_{22} & \partial r_3/\partial x_{23} \\
\partial R_1/\partial x_{11} & \partial R_1/\partial x_{12} & \partial R_1/\partial x_{13} & \partial R_1/\partial x_{21} & \partial R_1/\partial x_{22} & \partial R_1/\partial x_{23} \\
\partial R_2/\partial x_{11} & \partial R_2/\partial x_{12} & \partial R_2/\partial x_{13} & \partial R_2/\partial x_{21} & \partial R_2/\partial x_{22} & \partial R_2/\partial x_{23} \\
\partial R_3/\partial x_{11} & \partial R_3/\partial x_{12} & \partial R_3/\partial x_{13} & \partial R_3/\partial x_{21} & \partial R_3/\partial x_{22} & \partial R_3/\partial x_{23}
\end{bmatrix} = 1 \, .
$$

I leave it as a good exercise (and not as hard as you might think) for you to show that substituting equations (4) and (5) in this and evaluating the determinant yields

$$
\alpha = \frac{m_1}{m_1 + m_2} = \frac{m_1}{M} \, .
$$

Then our change of variables becomes

$$
\mathbf{r} = \mathbf{x}_1 - \mathbf{x}_2 \tag{6a}
$$

$$
\mathbf{R} = \frac{m_1 \mathbf{x}_1 + m_2 \mathbf{x}_2}{M} \tag{6b}
$$

which are the familiar CM coordinates as claimed.

Putting this all together we have

$$
\frac{1}{m_1}\boldsymbol{\nabla}_1^2 + \frac{1}{m_2}\boldsymbol{\nabla}_2^2 = \frac{1}{\mu}\boldsymbol{\nabla}_r^2 + \frac{1}{M}\boldsymbol{\nabla}_R^2
$$

and hence the Schrödinger equation (3) becomes

$$
\left[-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}_r^2 - \frac{\hbar^2}{2M}\boldsymbol{\nabla}_R^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}) \, . \tag{7}
$$

This is clearly separable by letting (in a somewhat sloppy notation) $\psi(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r})\phi(\mathbf{R})$ which results in

$$
\frac{1}{\psi(\mathbf{r})}\left[-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}_r^2 + V(\mathbf{r}) \right]\psi(\mathbf{r}) = E - \frac{1}{\phi(\mathbf{R})}\left[-\frac{\hbar^2}{2M}\boldsymbol{\nabla}_R^2\phi(\mathbf{R}) \right] \, .
$$

Again, the left and right sides of this equation depend solely on different variables and so must be constant. This yields the two equations

$$
\left[-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}_r^2 + V(\mathbf{r}) \right]\psi(\mathbf{r}) = E_r\psi(\mathbf{r}) \tag{8a}
$$

and

$$
-\frac{\hbar^2}{2M}\boldsymbol{\nabla}_R^2\phi(\mathbf{R}) = E_R\phi(\mathbf{R}) \tag{8b}
$$

3

with

$$E = E_r + E_R\,.$$

This expresses the total energy as the sum of the translational center-of-mass energy plus the energy of relative motion. We can always choose $E_R = 0$ as defining our zero of energy.

Equation (8a) is the starting point for the solution to the hydrogen atom problem you solved in 130A, although you unknowingly may have approximated the reduced mass μ by the electron mass m_e. This is a pretty good approximation since the proton mass m_p is roughly 2000 times the electron mass, so if $m_e \ll m_p$, then $\mu = m_e m_p / (m_e + m_p) \approx m_e$.

2 Identical Particles and Exchange Degeneracy

In classical mechanics, it is possible to distinguish between identical particles by following their distinct trajectories without disturbing them in any way. As a result, exchanging the particles results in a physically distinct configuration. However, in quantum mechanics there is no such thing as a continuous trajectory, and hence there is no physical basis for distinguishing between identical particles. This means that two systems that differ only by the exchange of identical particles must be described by the same state vector.

So, by **identical particles**, we mean particles which are *completely and fundamentally* indistinguishable. There is no physical significance attached to the labeling of such particles, and there is no observable effect if any two of them are interchanged. As a consequence, the coordinates of such particles must enter into the Hamiltonian in *exactly* the same way. (In fact, Feynman once said that the reason electrons were indistinguishable was that there was really only one electron in the universe. By allowing this one electron to travel forward and backward in time, a single time slice at a given instant would show the existence of many identical electrons at different locations.)

For example, consider two noninteracting identical particles moving under the influence of some external force. Since each particle feels the same potential, the Hamiltonian must be of the form

$$H = \frac{\mathbf{p_1}^2}{2m} + \frac{\mathbf{p_1}^2}{2m} + V(\mathbf{x}_1) + V(\mathbf{x}_2)\,.$$

The stationary state solutions are then

$$\psi_{kl}(\mathbf{x}_1, \mathbf{x}_2) = \psi_k(\mathbf{x}_1)\psi_l(\mathbf{x}_2) \tag{9}$$

and the corresponding energy is

$$E_{kl} = E_k + E_l$$

where $H_{sp}\psi_k = E_k\psi_k$ and H_{sp} is the single particle Hamiltonian

$$H_{sp} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x})$$

4

common to both particles. If k and l are different, the state ψ_{kl} is degenerate with respect to the interchange of the particles, and hence the state $\psi_{kl} = \psi_k(\mathbf{x}_1)\psi_l(\mathbf{x}_2)$ must have the same energy as the state $\psi_{lk} = \psi_l(\mathbf{x}_1)\psi_k(\mathbf{x}_2)$. This degeneracy is called **exchange degeneracy**, and is a consequence of the invariance of H under the exchange of the coordinates of the two particles.

Let us show that this exchange degeneracy is a property of the solutions to Schrödinger's equation for *any* system of identical particles, independently of the number of particles present or the forces they may be moving under. To do this, we define the **exchange operator** $P_{ij} = P_{ji}$ which exchanges the coordinates of particles i and j when acting on any function of those coordinates:

$$P_{ij}f(x_1,\ldots,x_i,\ldots,x_j,\ldots,x_N) = f(x_1,\ldots,x_j,\ldots,x_i,\ldots,x_N).$$

In particular, note for example, that

$$\begin{aligned}
P_{12}P_{13}f(x_1,x_2,x_3,\ldots,x_N) &= P_{12}f(x_3,x_2,x_1,\ldots,x_N) \\
&= f(x_3,x_1,x_2,\ldots,x_N).
\end{aligned}$$

It is very important to note that this example also shows that P_{12} and P_{13} do not commute, as we easily see from

$$\begin{aligned}
P_{13}P_{12}f(x_1,x_2,x_3,\ldots,x_N) &= P_{13}f(x_2,x_1,x_3,\ldots,x_N) \\
&= f(x_2,x_3,x_1,\ldots,x_N).
\end{aligned}$$

And in general, for $N \geq 3$ we find that P_{ij} and P_{ik} will not commute. (However, it may very well be that P_{ij} and P_{kl} *will* commute if $i \neq j \neq k \neq l$.) What this example also shows is that the subscript on a coordinate labels the particle to which the coordinate refers, and not the order in which a coordinate appears in the function.

As discussed above, since the coordinates of all identical particles appear in the Hamiltonian in exactly the same way, it follows that H and P_{ij} must commute. Then if $\psi_E(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ is an eigenfunction of H with eigenvalue E, then

$$H(P_{ij}\psi_E) = P_{ij}H\psi_E = E(P_{ij}\psi_E)$$

and hence these states are degenerate with respect to the interchange of the ith and jth particles (unless $P_{ij}\psi_E$ is a multiple of ψ_E as it would be, for example, in the case where $\psi_{rr} = \psi_r(\mathbf{x}_1)\psi_r(\mathbf{x}_2)$). Since the coordinates of N particles can be permuted in $N!$ ways, we now see that the solutions to the Schrödinger equation for N identical particles can be as much as $N!$-fold degenerate. Furthermore, these $N!$ states form a complete set, and any linear combination of a linearly independent subset of these is also a solution. Thus, in general, the classification of these solutions is a difficult problem. However, in the case of only two particles there is a complete solution to the problem.

For simplicity, let me change notation and denote the system with particle 1 in state a and (identical) particle 2 in state b by $|ab\rangle$. Since the particles are identical,

the states $|ab\rangle$ and $|ba\rangle$ describe the same physical situation, and hence they can only differ by a phase. Thus we write

$$|ba\rangle = c|ab\rangle$$

with $|c| = 1$. Assuming no other degeneracies, the two states $|ab\rangle$ and $|ba\rangle$ span the space of possible states of our system (corresponding to a particular eigenvalue of some observable). Since there is no way to tell which particle is in which state, an arbitrary solution to the Schrödinger equation is of the form

$$|\psi\rangle = \alpha|ab\rangle + \beta|ba\rangle = (\alpha + c\beta)|ab\rangle \tag{10}$$

where α, β are complex numbers.

Let λ be an eigenvalue of the exchange operator P: $P|ab\rangle = \lambda|ab\rangle$. Then on the one hand

$$P^2|ab\rangle = \lambda P|ab\rangle = \lambda^2|ab\rangle$$

while on the other hand

$$P^2|ab\rangle = P|ba\rangle = |ab\rangle\,.$$

Thus the eigenvalues of P are $\lambda = \pm 1$ and

$$P|\psi\rangle = \pm|\psi\rangle\,.$$

For the case with $\lambda = +1$, applying P to $|\psi\rangle$ and using (10) we have

$$P|\psi\rangle = P(\alpha|ab\rangle + \beta|ba\rangle) = \alpha|ba\rangle + \beta|ab\rangle = (c\alpha + \beta)|ab\rangle$$

$$\equiv |\psi\rangle = (\alpha + c\beta)|ab\rangle$$

and hence $c\alpha + \beta = \alpha + c\beta$ which is equivalent to $\alpha = \beta$. Thus, up to an overall normalization, the eigenfunction of P with eigenvalue $+1$ is the state $|\psi_s\rangle$ defined by

$$|\psi_s\rangle = |ab\rangle + |ba\rangle\,.$$

For the case with $\lambda = -1$ we have

$$P|\psi\rangle = P(\alpha|ab\rangle + \beta|ba\rangle) = \alpha|ba\rangle + \beta|ab\rangle = (c\alpha + \beta)|ab\rangle$$

$$\equiv -|\psi\rangle = -(\alpha + c\beta)|ab\rangle$$

so that $c\alpha + \beta = -\alpha - c\beta$ and this implies $\alpha = -\beta$. Thus (again up to an overall normalization) the eigenfunction of P with eigenvalue -1 is the state $|\psi_a\rangle$ defined by

$$|\psi_a\rangle = |ab\rangle - |ba\rangle\,.$$

Since the states $|a\rangle$ and $|b\rangle$ are assumed to be orthonormal (they're the normalized eigenstates of some Hermitian operator) and $|ab\rangle = |a\rangle|b\rangle$, it is easy to see that

the normalized eigenstates of the exchange operator for two identical particles are the states

$$|\psi_s\rangle = \frac{1}{\sqrt{2}}(|ab\rangle + |ba\rangle) \tag{11a}$$

$$|\psi_a\rangle = \frac{1}{\sqrt{2}}(|ab\rangle - |ba\rangle). \tag{11b}$$

The state $|\psi_s\rangle$ is called the **symmetric** state, and the state $|\psi_a\rangle$ is called the **antisymmetric** state under exchange. This shows that the states of two identical particles can always be classified according to their behavior under exchange. For example, the states (9) of two non-interacting particles yield the *correlated* states

$$\psi_{kl}^\pm = \frac{1}{\sqrt{2}}[\psi_k(\mathbf{x}_1)\psi_l(\mathbf{x}_2) \pm \psi_l(\mathbf{x}_1)\psi_k(\mathbf{x}_2)].$$

Note that

$$P\psi_{kl}^\pm = \pm\psi_{kl}^\pm$$

as is should.

(*Remark:* Don't confuse the property of being symmetric or antisymmetric under exchange with being even or odd under parity (i.e., spatial inversion $\mathbf{x} \to -\mathbf{x}$). The function $x_1 + x_2$ is symmetric under exchange, but odd under parity, while $x_1{}^2 + x_2{}^2$ is symmetric under exchange and even under parity.)

Example 1. Consider two identical coupled one-dimensional harmonic oscillators. The Hamiltonian for this system is

$$H = \frac{p_1{}^2}{2m} + \frac{p_2{}^2}{2m} + \frac{1}{2}m\omega^2 x_1{}^2 + \frac{1}{2}m\omega^2 x_2{}^2 + \frac{1}{2}k(x_1 - x_2)^2$$

and transforming to center-of-mass coordinates

$$X = \frac{x_1 + x_2}{2} \qquad \text{and} \qquad x = x_1 - x_2$$

we have

$$H = \frac{P^2}{2M} + \frac{1}{2}M\omega^2 X^2 + \frac{p^2}{2\mu} + \frac{1}{2}\mu\bar\omega^2 x^2$$

where $M = 2m$, $\mu = m/2$ and $\bar\omega^2 = \omega^2 + k/\mu = \omega^2 + 2k/m$.

The stationary state solutions are

$$\Psi_{kl} = \Phi_k(X)\phi_l(x) = \Phi_k\left(\frac{x_1 + x_2}{2}\right)\phi_l(x_1 - x_2)$$

where you will recall that the harmonic oscillator solutions $\phi_l(x)$ are proportional to $H_n(\xi)e^{-\xi^2/2}$ and where the Hermite polynomials H_n are even or odd depending on whether n is even or odd. Therefore

$$P\Psi_{kl} = (-1)^l\Psi_{kl} \tag{12}$$

so that these states are automatically symmetrized.

Now what happens if our system consists of $N \geq 3$ particles? The Hamiltonian for a system of N identical particles moving under a common external potential and interacting under a mutual interaction is of the form

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^{N} V(\mathbf{x}_i) + \sum_{i<j} \widetilde{V}(|\mathbf{x}_i - \mathbf{x}_j|). \tag{13}$$

This Hamiltonian is clearly invariant under any P_{ij}. However, as we saw above, P_{ij} and P_{kl} will not commute in general, and hence H, P_{ij} and P_{kl} do not form a mutually commuting set of operators. Therefore, in general we *can not* simultaneously specify the symmetry of a state function under the exchange of both the ith and jth particles as well as the kth and lth. In other words, the solutions to the Schrödinger equation for a system of three or more identical particles do not have a definite symmetry with respect to the exchange of each and every pair of particles. However, there are two important exceptions to this. First, a bit of notation.

I will denote the set of all permutations of N objects by S_N. (The notation really stands for the symmetric group of order N.) It should be obvious that S_N contains $N!$ members. It is a fact (but not so easy to prove formally) that any given permutation can be written as a (not necessarily unique) product of transpositions (i.e., the exchange of two objects), but that the number of such transpositions is uniquely either even or odd. Thus it makes sense to talk about the **sign** of a permutation as being either even or odd. We write $\operatorname{sgn} \sigma$ to denote the number $(-1)^r$ where r is the number of transpositions in σ. We will denote the members of S_N by a Greek letter such as σ. Thus, under $\sigma \in S_N$, the ordered set $(x_1, x_2, \ldots, x_N)$ becomes the ordered set $(x_{\sigma 1}, x_{\sigma 2}, \ldots, x_{\sigma N})$ where $(\sigma 1, \sigma 2, \ldots, \sigma N)$ is just $(1, 2, \ldots, N)$ taken in the new permuted order.

Let us denote the unsymmetrized eigenstates of (13) by $\psi_E(\mathbf{x}_1, \ldots, \mathbf{x}_N)$. Then the **totally symmetric state** Ψ_E^+ is the eigenstate of H defined by

$$\Psi_E^+ = \sum_{\sigma \in S_N} \psi_E(\mathbf{x}_{\sigma 1}, \mathbf{x}_{\sigma 2}, \ldots, \mathbf{x}_{\sigma N}) \tag{14a}$$

and the **totally antisymmetric state** Ψ_E^- is the state

$$\Psi_E^- = \sum_{\sigma \in S_N} (\operatorname{sgn} \sigma) \psi_E(\mathbf{x}_{\sigma 1}, \mathbf{x}_{\sigma 2}, \ldots, \mathbf{x}_{\sigma N}). \tag{14b}$$

The states $\Psi_E^\pm$ now have the property that for any i, j we have

$$P_{ij} \Psi_E^\pm = \pm \Psi_E^\pm.$$

In summary, we have shown that with the exception of the totally symmetric and antisymmetric states (14), the exchange-degenerate multi-particle states (which may be as much as $N!$-fold degenerate) possess no definite symmetry. Fortunately, most of these $N!$ states do not occur in nature, as we now discuss.

We have seen that all elementary particles have an intrinsic angular momentum which we call spin. This spin takes on values that are integral or half-odd-integral

multiples of $\hbar$ (including 0). In order to specify the state of our system, we must not only specify the external coordinates of each particle, but we must also specify the spin, which we view as the *internal* coordinates of the particle. If by the exchange of coordinates we mean the exchange of both internal and external coordinates, then all of the above discussion on exchange degeneracy remains unchanged, and the $N!$-fold degeneracy may still occur.

However, nature has decreed that only one of the $N!$ states is ever observed for a given type of particle. In particular, *the state function for a system of integer spin particles is always totally symmetric, and the state function for a system of half-odd-integer spin particles is always totally antisymmetric.* The statement that the state function for a system of half-odd-integer spin particles must be totally antisymmetric is called the **Pauli exclusion principle**. This is a more general version of the elementary statement you have probably heard that no two electrons can occupy the same atomic state.

Now note that a completely equivalent way to write Ψ_E^- is (see the sections on the Levi-Civita symbol and on determinants in the handout *Supplementary Notes on Mathematics*)

$$\Psi_E^- = \varepsilon^{i_1 i_2 \cdots i_N} \psi_E(\mathbf{x}_{i_1}, \mathbf{x}_{i_2}, \ldots, \mathbf{x}_{i_N}). \tag{15a}$$

If we have a system of N non-interacting particles, then the stationary state wave function is a product of N single-particle wave functions (see equation (9)), and the totally antisymmetric state is then

$$\Psi_E^- = \varepsilon^{i_1 i_2 \cdots i_N} \psi_{n_1}(\mathbf{x}_{i_1}) \psi_{n_2}(\mathbf{x}_{i_2}) \cdots \psi_{n_N}(\mathbf{x}_{i_N}) \tag{15b}$$

where $\sum_{i=1}^N E_{n_i} = E$. Note that this is just the determinant of a matrix whose (j,k)th entry is $\psi_{n_j}(\mathbf{x}_k)$. Such a determinant is called a **Slater determinant**. Written out and including the internal spin coordinate, the normalized antisymmetric state is

$$\Psi_E^- = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{n_1}(\mathbf{x}_1, s_1) & \psi_{n_1}(\mathbf{x}_2, s_2) & \cdots & \psi_{n_1}(\mathbf{x}_N, s_N) \\ \psi_{n_2}(\mathbf{x}_1, s_1) & \psi_{n_2}(\mathbf{x}_2, s_2) & \cdots & \psi_{n_2}(\mathbf{x}_N, s_N) \\ \vdots & \vdots & & \vdots \\ \psi_{n_N}(\mathbf{x}_1, s_1) & \psi_{n_N}(\mathbf{x}_2, s_2) & \cdots & \psi_{n_N}(\mathbf{x}_N, s_N) \end{vmatrix}.$$

Note that the product of the diagonal elements gives the original unsymmetrized state, and the rest of the terms generate a complete set of all permutations including the proper sign. For this case of noninteracting particles, we see that if any two particles are in the same spatial and spin state, then the total wave function vanishes since in this case the determinant would have two identical rows. Thus the Slater determinant provides a mathematical formulation of the Pauli exclusion principle for single-particle wave functions.

In statistical mechanics, particles with integer spin obey Bose-Einstein statistics, and are called **bosons**, while particles with half-odd-integer spin obey Fermi-Dirac statistics and are called **fermions**. These two classes of particles have radically

different macroscopic properties. For example, the exclusion principle applied to electrons is the main reason that a white dwarf doesn't collapse under its own gravitational force. (At least as long as its mass is less than 1.4 solar masses. If the mass is greater, then a neutron star forms due to inverse beta decay $p + e \rightarrow n + \nu$ which uses up the electrons to form neutrons. Now the neutrons form a highly degenerate Fermi gas, and their degeneracy pressure will support the star as long as the mass is less than about 3 solar masses. If the mass is larger, further collapse will occur and a black hole will form. We will calculate this degeneracy pressure in Section 3.)

The wave function symmetry requirement also applies to a system containing two or more identical composite particles. For example, consider the $^{16}O_2$ molecule. The oxygen nucleus contains 8 protons and 8 neutrons, each of which is a spin 1/2 fermion. Therefore, if we interchange the nuclei we interchange 16 fermions, and hence the wave function must be multiplied by a factor of $(-1)^{16} = 1$. This shows that the $^{16}O_2$ molecular wave function must be symmetric with respect to the interchange of nuclear coordinates. So in general, if we interchange two identical composite particles containing m identical bosons and n identical fermions, the wave function is multiplied by $(+1)^m(-1)^n = (-1)^n$. Thus *a composite particle is a fermion if it contains an odd number of fermions, and is a boson if it contains an even number of fermions.*

The reduction from $N!$ exchange degenerate states to a single state is as far as we can go for particles without spin. For example, consider the coupled harmonic oscillators in Example 1. Since these are spinless particles, the state function must be symmetric under exchange, and hence from (12) we see that only states with even l are physically realistic. Thus only half of the *mathematical* (and perfectly well behaved) solutions to Schrödinger's equation are also *physical* solutions.

What about spin one-half particles such as electrons? Noting that the (non-relativistic) Hamiltonian is usually independent of spin, it follows that the spin operator for each particle commutes with H so that each particle's spin is a constant of the motion. As a consequence, any solution to the spin-independent Schrödinger equation remains a solution even when multiplied by an arbitrary function of spin, and the general solution is then of the form

$$\Psi = \psi(\mathbf{x})\chi(\mathbf{s})\,.$$

In other words, the presence of spin introduces an additional degeneracy in the solutions. For example, ψ could be a one-electron atomic orbital (a one-electron spatial wave function is called an **orbital**, and an orbital for an electron in an atom is called an **atomic orbital**) and χ a one-electron spin function. Product functions of this type are called **spin-orbitals**.

What are the electronic configurations of elements in the periodic table? Recall that the hydrogenlike orbitals ψ_{nlm} are characterized by the quantum numbers $n = 1, 2, 3, \ldots$, $l = 0, 1, 2, \ldots, n-1$ and $m_l = 0, \pm 1, \pm 2, \ldots, \pm l$. An alternative notation is to denote the value of l by a letter:

l	0	1	2	3	4	5	6	7
letter	s	p	d	f	g	h	i	k

The letters s, p, d, f are of spectroscopic origin, and stand for sharp, principle, diffuse and fundamental. After f we proceed alphabetically with the exception of j which is omitted. Preceding the letter that represents l we write the value of n so, for example, the ground state wave function ψ_{100} is simply denoted by $1s$. For $n = 2$ we have the states ψ_{200}, ψ_{210} and $\psi_{21\pm1}$. The state ψ_{200} is denoted $2s$, and the three $2p$ states are given an additional subscript that denotes the m_l value, so we write $2p_0$, $2p_1$ and $2p_{-1}$. (While we won't go into any detail, chemists generally use states that are *real* linear combinations of these *complex* m_l-value states (the spherical harmonics contain a factor $e^{im_l\phi}$), so you will frequently see wave functions such as $2p_x$, $2p_y$ and $2p_z$. This is valid because the energy of the hydrogen atom eigenfunctions is independent of m_l, so linear combinations of states with the same n and l values but different m_l values are also eigenfunctions with the same energy.)

Two electrons (one with spin up and one with spin down) can fill the lowest $n = 1$, $l = 0$ energy states, so a hydrogen atom with one electron in its ground state has the electronic configuration denoted $1s$, and a helium atom with two electrons in their lowest states has the configuration $1s^2$. Next is lithium with three electrons and the ground state configuration $1s^2 2s$. Boron has five electrons which fill the $n = 1$, $l = 0$ states and occupy (some of) the $n = 2$, $l = 0, 1$ states, so its ground state configuration is $1s^2 2s^2 3p$.

It should be clear how to continue this process to deduce the electronic configurations of the lightest elements. However, this doesn't work with heavier elements because the actual relative energy levels of the wave functions change with varying Z. (The Hamiltonian in (28) is only an approximation that neglects other terms such as spin–orbit coupling and relativistic effects.) More detailed calculations show that in hydrogen, the $3d$ orbital lies below the $4s$ orbital as you would expect, but for $7 \leq Z \leq 20$ it turns out that the $4s$ orbital lies below the $3d$. Then at large values of Z the $3d$ is again lower. This is due in large part to complex screening effects of the inner orbitals.

Keep in mind however, that the symmetry requirements for fermions and bosons refer to the entire wave function and not to either the spatial or spin parts alone, and thus there are in general many ways to achieve the correct symmetry. In a simple case such as two electrons, we can construct an antisymmetric wave function by multiplying a symmetric spatial function by an antisymmetric spin state, or we can use an antisymmetric spatial state with a symmetric spin function. As we have seen, the antisymmetric singlet state is spin zero, and the symmetric triplet state is spin one. Again referring to the coupled harmonic oscillators, we see that if they are spin one-half particles such as electrons, then in fact all mathematical solutions are also physically realizable, because for l even we have the spin zero state, and for l odd the spin one state.

Example 2. Let us look at the helium atom taking into account electron spin and the exclusion principle. If we assume an infinitely heavy nucleus and neglect electron-electron repulsion and other interactions, then the helium atom Hamiltonian becomes simply the sum of two hydrogen atom Hamiltonians, and the wave

function is easily written as a product of two hydrogenlike orbitals. Thus, in this simple model, we take the "zeroth-order" ground state $\psi^{(0)}$ to be $1s^2$. We will write this as $1s(1)1s(2)$ where the number in parenthesis denotes which electron we are talking about (as if they were distinguishable).

To take spin into account, we must multiply this spatial function by spin eigenfunction. We have already seen that the possible spin states for two electrons are

$$\text{triplet symmetric states:} \quad \begin{cases} |1\ 1\rangle = |+\ +\rangle \\ |1\ 0\rangle = 2^{-1/2}\{|+\ -\rangle + |-\ +\rangle\} \\ |1\ -1\rangle = |-\ -\rangle \end{cases}$$

$$\text{singlet antisymmetric state:} \quad |0\ 0\rangle = 2^{-1/2}\{|+\ -\rangle - |-\ +\rangle\}\,.$$

where, for example, $|+\ -\rangle$ is a shorthand notation for $|1/2\ -1/2\rangle$. Since the zeroth-order spatial wave function $\psi^{(0)} = 1s(1)1s(2)$ is symmetric with respect to exchange and the overall wave function must be antisymmetric, we must multiply the spatial wave function by an antisymmetric spin function. There is only one such possibility for two electrons, and hence the zeroth-order ground state wave function for the helium atom including spin is

$$\Psi^{(0)} = 1s(1)1s(2) \cdot 2^{-1/2}\{|+\ -\rangle - |-\ +\rangle\}\,.$$

Clearly, $P_{12}\Psi^{(0)} = -\Psi^{(0)}$ as it should.

Now let us take a more careful look at how the symmetrization requirement leads to a "force," although it isn't a force in the usual sense of the word. We consider two identical particles in a one-dimensional system. Using the same notation I used in constructing the eigenfunctions of the exchange operator P, we know that two identical bosons will be in the state (11a)

$$|\psi_s\rangle = \frac{1}{\sqrt{2}}(|ab\rangle + |ba\rangle)$$

and two identical fermions will be in the state (11b)

$$|\psi_a\rangle = \frac{1}{\sqrt{2}}(|ab\rangle - |ba\rangle)\,.$$

What we will show is that these two states lead to very different spatial probability distributions for total particle density. To see this, we will calculate the expectation value of the distance squared between the particles:

$$\langle(x_1 - x_2)^2\rangle = \langle x_1{}^2 + x_2{}^2 - 2x_1 x_2\rangle = \langle x_1{}^2\rangle + \langle x_2{}^2\rangle - 2\langle x_1 x_2\rangle\,. \tag{16}$$

As a first observation, note that if the particles were distinguishable, then it would make sense to talk about the two-particle state $|ab\rangle$ as that state in which

12

particle 1 is in the single particle state $|1; a\rangle$ (in what should be an obvious notation), and particle 2 is in the single particle state $|2; b\rangle$. In this case we have (assuming the one-particle states are normalized)

$$\langle x_1{}^2\rangle = \langle ab|x_1{}^2|ab\rangle = \langle 1; a|x_1{}^2|1; a\rangle\langle 2; b|2; b\rangle = \langle x^2\rangle_a$$

$$\langle x_2{}^2\rangle = \langle ab|x_2{}^2|ab\rangle = \langle 1; a|1; a\rangle\langle 2; b|x_2{}^2|2; b\rangle = \langle x^2\rangle_b$$

$$\langle x_1 x_2\rangle = \langle ab|x_1 x_2|ab\rangle = \langle 1; a|x_1|1; a\rangle\langle 2; b|x_2|2; b\rangle = \langle x\rangle_a\langle x\rangle_b$$

and therefore (16) becomes

$$\langle(x_1 - x_2)^2\rangle_{dp} = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b \tag{17}$$

where the subscript dp means distinguishable particles.

Now let us see what the consequences are of the symmetrization requirement for bosons and fermions. Using equations (11) together with the fact that $\langle a|b\rangle = 0$ we have

$$\langle x_1{}^2\rangle = \frac{1}{2}\langle ab \pm ba|x_1{}^2|ab \pm ba\rangle$$

$$= \frac{1}{2}\left[\langle ab|x_1{}^2|ab\rangle \pm \langle ab|x_1{}^2|ba\rangle \pm \langle ba|x_1{}^2|ab\rangle + \langle ba|x_1{}^2|ba\rangle\right]$$

$$= \frac{1}{2}\left[\langle x^2\rangle_a \pm 0 \pm 0 + \langle x^2\rangle_b\right]$$

$$= \frac{1}{2}\left[\langle x^2\rangle_a + \langle x^2\rangle_b\right] .$$

It should be clear that we also have

$$\langle x_2{}^2\rangle = \frac{1}{2}\left[\langle x^2\rangle_b + \langle x^2\rangle_a\right] .$$

And for the mixed product we find

$$\langle x_1 x_2\rangle = \frac{1}{2}\langle ab \pm ba|x_1 x_2|ab \pm ba\rangle$$

$$= \frac{1}{2}\left[\langle ab|x_1 x_2|ab\rangle \pm \langle ab|x_1 x_2|ba\rangle \pm \langle ba|x_1 x_2|ab\rangle + \langle ba|x_1 x_2|ba\rangle\right]$$

$$= \frac{1}{2}\left[\langle x\rangle_a\langle x\rangle_b \pm \langle a|x|b\rangle\langle b|x|a\rangle \pm \langle b|x|a\rangle\langle a|x|b\rangle + \langle x\rangle_b\langle x\rangle_a\right]$$

$$= \langle x\rangle_a\langle x\rangle_b \pm |\langle a|x|b\rangle|^2 .$$

Putting these results together, (16) becomes

$$\langle(x_1 - x_2)^2\rangle_\pm = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b \mp 2|\langle a|x|b\rangle|^2 . \tag{18}$$

13

Now, comparing (17) to (18) we see that

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle (x_1 - x_2)^2 \rangle_{dp} \mp 2 \left| \langle a|x|b \rangle \right|^2 . \tag{19}$$

Thus we see that for bosons (the symmetric case), the expectation value of the particle separation will be less than it is for distinguishable particles, and for fermions (the antisymmetric case), the particle separation will be greater than that for distinguishable particles (all in the same state of course). Note that the distinguishable and indistinguishable situations are the same if the overlap integral $\langle a|x|b \rangle$ vanishes. In other words, if the particles are well separated, they may be treated as if they are distinguishable.

Summarizing, equation (19) shows that identical bosons tend to behave as if there were a force of attraction between particles, and identical fermions behave as if there were a repulsive force between particles. This apparent force is called an **exchange force**, although you should realize that it is not a fundamental force at all, but rather a mathematical consequence of the symmetrization requirement for identical particles.

Example 3. Let me illustrate the necessity of symmetrizing or antisymmetrizing the state of identical particles. Consider two fictional non-interacting electrons in a one-dimensional infinite square box potential

$$V(x) = \begin{cases} 0 & -L/2 < x < L/2 \\ \infty & \text{otherwise} \end{cases} .$$

The time-independent Schrödinger equation for this system inside the well is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x_1, x_2)}{\partial x_1{}^2} - \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x_1, x_2)}{\partial x_2{}^2} = E\psi(x_1, x_2)$$

and this is easily solved by separation of variables. Each particle has a solution of the form (with $k^2 = 2mE/\hbar^2$)

$$\psi(x) = a \sin kx + b \cos kx$$

and the boundary conditions are

$$0 = \psi(L/2) = a \sin kL/2 + b \cos kL/2$$

and

$$0 = \psi(-L/2) = -a \sin kL/2 + b \cos kL/2 .$$

Adding these implies $b \cos kL/2 = 0$, and subtracting yields $a \sin kL/2 = 0$.

If $b = 0$ then we must have $\sin kL/2 = 0$ (we don't want $a = 0$ also) and hence $kL/2 = n\pi$ or $k = 2n\pi/L$. Since $2n$ is always an even integer, we can write these solutions as

$$\psi_n(x) = a \sin(n\pi x/L) \qquad \text{for } n \text{ even} .$$

14

If $b \neq 0$ then $\cos kL/2 = 0$ so that $kL/2 = n\pi/2$ for n odd. This is the same as $k = n\pi/L$ for n odd, and hence the second set of solutions is

$$\psi_n(x) = b\cos(n\pi x/L) \qquad \text{for } n \text{ odd}.$$

(We will see later in the course that because the potential is symmetric, the solutions to the Schrödinger equation may be chosen to have a definite symmetry. Hence the solutions will be either even or odd as we just saw.)

A possible complete solution for n_1 a positive even integer and n_2 a positive odd integer is now

$$\psi_{n_1 n_2}(x_1, x_2) = A\sin(n_1\pi x_1/L)\cos(n_2\pi x_2/L) \qquad (20\text{a})$$

with

$$E = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(n_1^2 + n_2^2).$$

Note that this has the same energy as the distinct solution

$$\psi_{n_2 n_1}(x_1, x_2) = A\sin(n_1\pi x_2/L)\cos(n_2\pi x_1/L). \qquad (20\text{b})$$

However, there is a problem with this. The number $|\psi(x_1, x_2)|^2\,dx_1 dx_2$ is the probability of finding electron 1 in the interval dx_1 and electron 2 in the interval dx_2. Consider the state (20a) with $n_1 = 2$ and $n_2 = 3$. The probability of finding electron 1 at $x_1 = 0$ and electron 2 at $x_2 = L/4$ is zero because $\psi = 0$ at $x_1 = 0$. On the other hand, the probability of finding electron 1 at $x_1 = L/4$ and electron 2 at $x_2 = 0$ is *not* zero. But the electrons are indistinguishable, so this result is not physically meaningful.

The resolution to this is the requirement that the probabilities must be such that

$$|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$$

which is certainly not satisfied by equations (20). However, both the symmetrized and antisymmetrized combinations

$$\psi_{n_1 n_2}^{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1 n_2}(x_1, x_2) \pm \psi_{n_1 n_2}(x_2, x_1)\right] \qquad (21)$$

will satisfy this requirement.

It is quite interesting to plot density contours of $\left|\psi_{n_1 n_2}^{\pm}(x_1, x_2)\right|^2$. For the symmetrized case $|\psi^+|^2$ we have
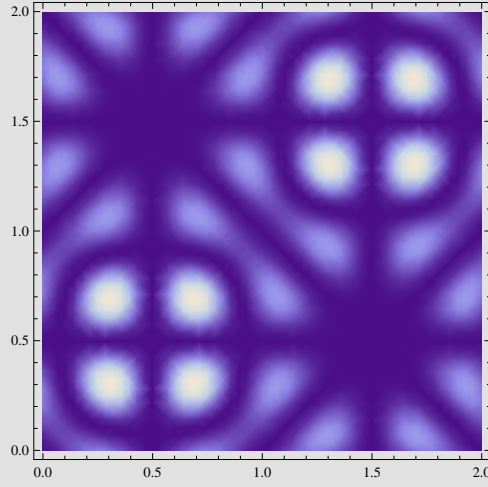
Figure 1: Density plot of $\left|\psi_{n_1 n_2}^+(x_1, x_2)\right|^2$.

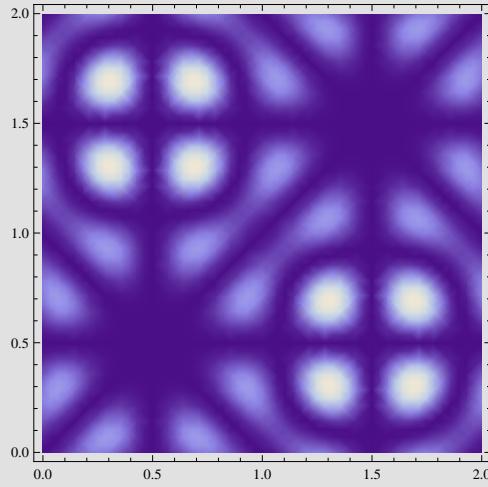and for the antisymmetrized case $|\psi^-|^2$ we have

Figure 2: Density plot of $\left|\psi_{n_1 n_2}^-(x_1, x_2)\right|^2$.

The difference between these plots is striking. In the case of $|\psi^+|^2$ we see that the greatest probability density lies in areas along the line $x_1 = x_2$, while for $|\psi^-|^2$ the probability is zero along this line. In other words, bosons are most likely to be found close together, whereas fermions will never be found in the same place, and in fact are localized far apart from each other.

3   Degeneracy Pressure

When a stellar core runs out of nuclear fuel, there is no longer any radiation pressure to support the star, and the core collapses, blowing away the outer layers in what is called a planetary nebula. If the core is less than a few solar masses, the endpoint of this collapse is a white dwarf. The density of the white dwarf is so high that the electrons form a highly degenerate Fermi gas, and the **degeneracy pressure** due to the exclusion principle is what continues to support the star. (However, the electrons are moving at relativistic speeds, so the laws of relativistic statistical mechanics must be used to work out the details.)

If the white dwarf has a mass greater than 1.4 solar masses (the so-called **Chandrasekhar limit**), then the density becomes so high that inverse beta decay occurs ($p+e \rightarrow n+\nu$) and the white dwarf becomes neutron rich. Without the electrons to provide the degeneracy pressure, the core collapses further to form a neutron star. Now the neutrons form a highly degenerate Fermi gas whose degeneracy pressure supports the star. (A typical neutron star is roughly one solar mass, but has a radius of the order 15 km.) The neutron star can exist only as long as its mass is less than about three solar masses. If its mass is greater than this, further collapse will occur to form a black hole.

As a simple model of this degeneracy pressure, let us consider an idealized gas consisting of a large number of *non-interacting* electrons in a rectangular infinite potential well

$$V(\mathbf{x}) = \begin{cases} 0 & \text{for } 0 < x < l_x,\ 0 < y < l_y,\ 0 < z < l_z \\ \infty & \text{outside the well} \end{cases}.$$

(Here I am following Griffiths, Section 5.3.1.) Inside the well we have the free time-independent Schrödinger equation in three dimensions

$$-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

which is easily solved by separation of variables as in Example 3. The solution is

$$\psi(\mathbf{x}) = X(x)Y(y)Z(z)$$

where

$$X(x) = A_x \sin k_x x + B_x \cos k_x x$$

and similarly for $Y(y)$ and $Z(z)$. Again, we have defined

$$k_x^2 = 2mE_x/\hbar^2$$

with similar equations for k_y and k_z, and we also have $E = E_x + E_y + E_z$.

Because the potential well is not symmetric about the origin, the solutions won't have a definite symmetry. Our boundary conditions are, for example, $X(0) = X(l_x) = 0$ so that $B_x = 0$ and $k_x l_x = n_x \pi$ or

$$k_x = \frac{n_x \pi}{l_x} \qquad n_x = 1, 2, 3, \ldots . \tag{22}$$

The complete, normalized solution is now (with $V = l_x l_y l_z$)

$$\psi(\mathbf{x}) = \sqrt{\frac{8}{V}} (\sin n_x \pi x / l_x)(\sin n_y \pi y / l_y)(\sin n_z \pi z / n_z)$$

and

$$E = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m} \tag{23}$$

where we have defined the **wave vector** $\mathbf{k} = (k_x, k_y, k_z)$. Since each component of $\mathbf{k}$ is greater than zero, the allowed energy states lie in the positive octant of $\mathbf{k}$-space. The two-dimensional case is easier to visualize, so we have the following situation:
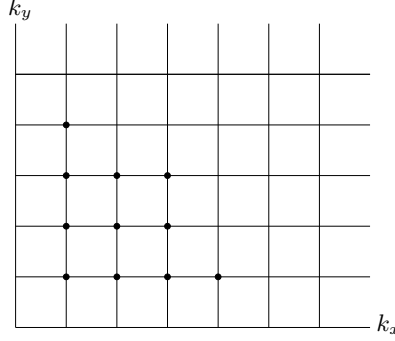
Noting that each $k_i \neq 0$, we see that as we go from one state to the next starting at the lowest energy level (i.e., $n_x = n_y = 1$), we increase the included area by one square (i.e., by one unit of area in $\mathbf{k}$-space), and the area of this square is $(\pi/l_x)(\pi/l_y) = \pi^2/l_x l_y$ (since n_i increases by 1 at each step). Therefore, generalizing to three dimensions, each state occupies a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} . \tag{24}$$

Now suppose that we start adding atoms to our well, where each atom contributes q free electrons. (So we are looking at a box containing a free electron gas.) Because of the exclusion principle, only two electrons can occupy any given energy state (one electron with spin up and one with spin down), so as we add them, we will fill one octant of a sphere in $\mathbf{k}$-space. (While this isn't truly a smooth sphere, it's close enough for our purposes.) The final radius k_F of the sphere will be such that all of the electron states have been included, and is given in terms of the total number N of particles as

$$\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{Nq}{2} \left(\frac{\pi^3}{V} \right)$$

where the factor of $1/8$ on the left is because we are only filling one octant in $\mathbf{k}$-space. The factor $Nq/2$ is the total number of states required for a particle of

spin 1/2, and π^3/V is the volume occupied per state. Defining the **free electron density**

$$\rho = \frac{Nq}{V}$$

the final radius k_F of the sphere is given by

$$k_F = (3\pi^2\rho)^{1/3}\,. \tag{25}$$

The surface of this sphere in **k**-space is called the **Fermi surface**, and the corresponding **Fermi energy** E_F is given by

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3}\,. \tag{26}$$

To calculate the total energy of the free electron gas, we first note that the volume of an octant in **k**-space is

$$V = \frac{1}{8}\left(\frac{4}{3}\pi k^3\right) = \frac{1}{6}\pi k^3$$

so that

$$dV = \frac{1}{2}\pi k^2\,dk\,.$$

The number of states contained in this volume element is (using (24)) $dV/(\pi^3/V) = V\,dV/\pi^3$, and since there are two electrons per state, the total number of electrons in the volume element dV is

$$2\frac{V\,dV}{\pi^3} = \frac{V}{\pi^2}k^2\,dk\,.$$

From equation (24) we know that each state has energy $\hbar^2 k^2/2m$, so the energy of the volume element is

$$\frac{\hbar^2 k^2}{2m}\frac{V}{\pi^2}k^2\,dk\,.$$

Integrating this from $k = 0$ to $k = k_F$ we obtain the total energy of the electrons occupying all of the states in the octant

$$E_{\text{tot}} = \frac{\hbar^2 V}{2\pi^2 m}\int_0^{k_F} k^4\,dk = \frac{\hbar^2 k_F^5}{10\pi^2 m}V = \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m}V^{-2/3}\,. \tag{27}$$

Now recall the first law of thermodynamics, $dE = dQ - PdV$, where dE is the change in energy of the system, dQ represents the heat added to the system, and PdV is the work done *by* the system. In the present case, we assume that $dQ = 0$, and hence $dE = -PdV$. From (27) we have

$$-P = \frac{dE_{\text{tot}}}{dV} = -\frac{2}{3}\frac{E_{\text{tot}}}{V}$$

so we see that the exclusion principle has led to an electron **degeneracy pressure**

$$P = \frac{2}{3}\frac{E_{\text{tot}}}{V} = \frac{2}{3}\frac{\hbar^2 k_F^5}{10\pi^2 m} = \frac{\hbar^2}{5m}(3\pi^2)^{2/3}\rho^{5/3}\,.$$

In other words, even in our idealized case of non-interacting electrons, there is an effective force of repulsion that is purely quantum mechanical and due to the required antisymmetry of the wave function for identical particles.

4   Many-Electron Atoms

The simplest Hamiltonian for an n-electron atom is

$$H = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Ze'^2}{r_i} + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{e'^2}{r_{ij}} \tag{28}$$

where

$$e' = \frac{e}{(4\pi\varepsilon_0)^{1/2}}$$

and we have assumed an infinitely heavy nucleus. This Hamiltonian consists of (1) the kinetic energies of the n electrons; (2) the potential energy of attraction between the electrons and a nucleus of charge Ze' (where $Z = n$ for a neutral atom); and (3) the potential energy of electron-electron repulsion (where the sum $j > i$ avoids double counting and terms like e'^2/r_{ii}). Equation (28) also neglects other terms such as spin–orbit interactions, but these are small in comparison. (We will treat some of these other terms when we discuss perturbation theory.)

The **total electronic orbital angular momentum** of an n-electron atom is defined as

$$\mathbf{L} = \sum_{i=1}^{n}\mathbf{L}_i\,.$$

It can be shown (see Bethe and Jackiw, *Intermediate Quantum Mechanics*) that even though each angular momentum operator $\hat{\mathbf{L}}_i$ fails to commute with the H of equation (28), the total angular momentum operator $\hat{\mathbf{L}}$ does commute, and hence we can describe an atomic state by the value of L, where

$$\hat{L}^2\Psi = L(L+1)\hbar^2\Psi$$

and Ψ is the electronic wave function of the atom. (In this section I will sometimes denote operators with a hat to distinguish them from either their classical counterparts or their corresponding eigenvalues.) Historically, spectroscopists denote the value of L for a given atom by a letter defined as follows:

L	0	1	2	3	4	5	6	7	8
letter	S	P	D	F	G	H	I	K	L

We will use capital letters to denote the total orbital angular momentum of an atom, and lower case letters to denote the orbital angular momentum of individual electrons.

Example 4. Consider a carbon atom (atomic number 6) with the electronic configuration $1s^2 2s^2 2p3d$. The s electrons have $l = 0$ so they don't contribute to the total angular momentum of the atom. The p electron has $l = 1$, and the d electron has $l = 2$. From our discussion of the addition of angular momentum, the possible values of L are then $L = 1, 2, 3$. Hence the $1s^2 2s^2 2p3d$ configuration gives rise to P, D and F states.

Similarly, we define the **total electronic spin angular momentum** to be the sum

$$\mathbf{S} = \sum_{i=1}^{n} \mathbf{S}_i \, .$$

Since the Hamiltonian (28) is independent of spin (we have ignored spin–orbit terms), it commutes with both $\hat{S}^2$ and $\hat{\mathbf{S}}_z$. However, this is not enough to conclude that the atomic wave functions Ψ are eigenstates of $\hat{S}^2$. This is because the antisymmetry requirement for electrons means that Ψ must be an eigenstate of the exchange operator P_{ij} with eigenvalue -1. Therefore P_{ij} must also commute with $\hat{S}^2$ if our states are to be simultaneous eigenstates of H, $\hat{S}^2$ and P_{ij}. Fortunately, from

$$S^2 = \mathbf{S} \cdot \mathbf{S} = (\mathbf{S}_1 + \mathbf{S}_2 + \cdots + \mathbf{S}_n) \cdot (\mathbf{S}_1 + \mathbf{S}_2 + \cdots + \mathbf{S}_n)$$

it is not hard to see that $[\hat{S}^2, P_{ij}] = 0$ (and similarly that $[\hat{L}^2, P_{ij}] = 0$) and hence our atomic wave functions are indeed eigenfunctions of $\hat{S}^2$. Thus we have

$$\hat{S}^2 \Psi = S(S+1)\hbar^2 \Psi$$

and the atomic states are characterized by the total electronic spin quantum number S.

Example 5. Again consider the electronic configuration $1s^2 2s^2 2p3d$ of Example 4, and let us find the possible values of S. First look at the two $1s$ electrons. Because of the exclusion principle we must have one electron with $m_s = +1/2$ and one with $m_s = -1/2$, so the z-component of the total spin of the $1s$ electrons can only be $M_S = 0$, and hence the total spin of the two $1s$ electrons can only be zero. This shows that while in general the addition of two spin $1/2$ particles yields total spin values $S = 0$ and $S = 1$, the additional restriction imposed by the exclusion principle (to the atomic orbitals) leaves $S = 0$ as the only possibility. Clearly the same argument applies to the two $2s$ electrons.

However, the exclusion principle does not apply to the $2p$ and $3d$ electrons since they're in different energy states. This means that the possible total spin states for

the $2p$ and $3d$ electrons are $S = 0$ and $S = 1$. Since the $1s$ and $2s$ electrons are in $S = 0$ states and don't contribute to the total spin, the possible total spin quantum numbers for the $1s^2 2s^2 2p3d$ configuration are $S = 0$ and $S = 1$.

Now, a given electronic configuration can in general give rise to several different atomic states that may or may not have the same energies. As an example, consider the first excited states of helium. (While we haven't covered perturbation theory yet, this is just a motivational example, so I will simply quote the result.) If we again neglect inter-electron repulsion (see Example 2), the "zeroth-order" lowest excited states have $n_1 = 1$ and $n_2 = 2$, or $n_1 = 2$ and $n_2 = 1$. But the $n = 2$ level of a hydrogenlike orbital is fourfold degenerate because the $2s$ and the three $2p$ states all have the same energy. Because of this, we must apply degenerate perturbation theory to find the correct zeroth-order wave functions, which are just linear combinations of the degenerate states.

The lowest excited state turns out to have the zeroth-order spatial wave function

$$2^{-1/2} \left[1s(1)2s(2) - 2s(1)1s(2) \right].$$

Since this is antisymmetric, we must multiply it by a two-electron symmetric spin function, so we have a triply degenerate level with the three zeroth-order wave functions

$$2^{-1/2} \left[1s(1)2s(2) - 2s(1)1s(2) \right] | + \, + \rangle$$
$$2^{-1/2} \left[1s(1)2s(2) - 2s(1)1s(2) \right] \cdot 2^{-1/2} \left\{ | + \, - \rangle + | - \, + \rangle \right\} \ . \qquad (29a)$$
$$2^{-1/2} \left[1s(1)2s(2) - 2s(1)1s(2) \right] | - \, - \rangle$$

The next excited state has the symmetric spatial wave function

$$2^{-1/2} \left[1s(1)2s(2) - 2s(1)1s(2) \right]$$

so multiplying by the antisymmetric two-electron spin function, the overall wave function must be

$$2^{-1/2} \left[1s(1)2s(2) + 2s(1)1s(2) \right] \cdot 2^{-1/2} \left\{ | + \, - \rangle - | - \, + \rangle \right\} \ . \qquad (29b)$$

In other words, the electronic configuration with one particle in an $n = 1$ state and another in an $n = 2$ state leads to triply degenerate states with one energy, and another singlet state with a different energy.

So we see that the atomic states that arise from a given electron configuration can be grouped into sets of states that have the same energy. It can be shown that (ignoring spin–orbit interactions) the states with the same energy that arise from the same electron configuration will have the same L and S values (see E.C. Kemble, *The Fundamental Principles of Quantum Mechanics*). Such a set of states is called an atomic **term**.

For a fixed value of L there are $2L + 1$ values of M_L, and for a fixed value of S there are similarly $2S + 1$ values of M_S. Since the atomic energies are independent

of M_L and M_S, the terms are thus $(2L+1)(2S+1)$-fold degenerate. (Again, this ignores spin–orbit interactions.) Each term of an atom is designated by a **term symbol** defined as

$$^{2S+1}L.$$

For example, a term with $L = 2$ and $S = 1$ has $2S + 1 = 3$ so the term symbol is written ^3D. The quantity $2S + 1$ is sometimes called the **electron-spin multiplicity** of the term. (Or simply the **multiplicity**.)

Example 6. Let us find the terms and degeneracies for the electron configuration $1s2p$. The $1s$ electron has $l = 0$, and the $2p$ electron has $l = 1$. Thus the only possible total value of L is $L = 1$, which is a P state. Each of the two electrons is spin $1/2$, so the total spin can be either $S = 0$ or $S = 1$, and hence the quantity $2S + 1$ can take the values $2S + 1 = 1, 3$. Therefore the possible terms are ^1P and ^3P.

The ^1P term has a degeneracy $(2L+1)(2S+1) = (3)(1) = 3$. These are obtained by replacing the $1s$ in (29b) by $2p_x$, $2p_y$ or $2p_z$. The ^3P term has a degeneracy $(2L+1)(2S+1) = (3)(3) = 9$, and these are also obtained by replacing the $2s$ in each of equations (29a) by $2p_x$, $2p_y$ or $2p_z$.

There are systematic ways of going about deriving the terms that arise from a given electron configuration. The easy situation is when there are only filled subshells. (The set of orbitals belonging to a given principle quantum number n is called a **shell**, and the set of orbitals belonging to a given n and a given l is called a **subshell**.) In this case, all electrons are paired up, so the only possible value for $M_S = \sum_i m_{s_i}$ is zero, and hence the only possible value of S is $S = 0$. Also, for each electron in a closed subshell with magnetic quantum number m_l, there is an electron with magnetic quantum number $-m_l$. (For example, the $2p^6$ configuration has two electrons with each of the values $m_l = 0$, $m_l = 1$ and $m_l = -1$.) Thus $M_L = \sum_i m_{l_i} = 0$ only, and we must have $L = 0$. Thus closed subshells give rise to only the term ^1S. *If the electron configuration consists of both open and closed subshells, the closed subshells do not contribute to L or S and may be ignored in finding the terms.*

Now consider two **nonequivalent** electrons; that is, two electrons in different subshells. Since these electrons must have different n and/or l values, there are no restrictions due to the exclusion principle. Therefore we find all possible values of L from the l_1 and l_2 values, and use these together with the possible S values which are only $S = 0, 1$ (i.e., the result of adding two spin one-half electrons). If there are more than two electrons, we combine the individual l values in the usual way to find the values of L, and combine the individual s values to find the values of S.

For example, consider a *pdf* configuration. The individual l values are $l = 1, 2, 3$, so adding $l = 1$ and $l = 2$ gives the possible values $L = 3, 2, 1$. Now adding in $l = 3$ to each of these we have the following sets of values for the total L:

$$6, 5, 4, 3, 2, 1, 0; \qquad 5, 4, 3, 2, 1; \qquad 4, 3, 2.$$

For spin we have to add three spin $1/2$ particles, so the first two give spins 1 and 0, and adding in the third yields the possible total spins $S = 3/2, 1/2, 1/2$ so that the possible values of the multiplicity are $2S + 1 = 4, 2, 2$. Now we combine *each* of the L values with *each* of the multiplicities. For example, there are three possibilities with $L = 4$. Combining these with a multiplicity 4 yields the term symbol $^4G(3)$ where the number in parenthesis is the number of times that particular term symbol occurs. Similarly, the multiplicity 2 occurs twice, so together with $L = 4$ we have $^2G(6)$. Continuing in this manner we obtain the following term symbols for the *pdf* configuration: $^2S(2)$, ^4S, $^2P(4)$, $^4P(2)$, $^2D(6)$, $^4D(3)$, $^2F(6)$, $^4F(3)$, $^2G(6)$, $^4G(3)$, $^2H(4)$, $^4H(2)$, $^2I(2)$, ^4I.

Electrons in the same subshell are called **equivalent** electrons. Since these have the same values of n and l, we must be sure than no two of them have all four of their quantum numbers the same. This means that not all of the terms derived for nonequivalent electrons will be possible. For example, consider two equivalent p electrons (such as the $2p^2$ electrons in the carbon atom configuration $1s^2 2s^2 2p^2$). The table below lists the possible values of m_l and m_s, along with M_L and M_S:

m_{l1}	m_{s1}	m_{l2}	m_{s2}	$M_L = m_{l1} + m_{l2}$	$M_S = m_{s1} + m_{s2}$
1	$\frac{1}{2}$	1	$-\frac{1}{2}$	2	0
1	$\frac{1}{2}$	0	$\frac{1}{2}$	1	1
1	$\frac{1}{2}$	0	$-\frac{1}{2}$	1	0
1	$-\frac{1}{2}$	0	$\frac{1}{2}$	1	0
1	$-\frac{1}{2}$	0	$-\frac{1}{2}$	1	-1
1	$\frac{1}{2}$	-1	$\frac{1}{2}$	0	1
1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	0	0
1	$-\frac{1}{2}$	-1	$\frac{1}{2}$	0	0
1	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	0	-1
0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0
0	$\frac{1}{2}$	-1	$\frac{1}{2}$	-1	1
0	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	0
0	$-\frac{1}{2}$	-1	$\frac{1}{2}$	-1	0
0	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	-1
-1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	0

The important point here is that a number of possible combinations are missing from this table. For example, there is no combination with $m_{l1} = 1$, $m_{s1} = 1/2$, $m_{l2} = 1$ and $m_{s2} = 1/2$ because this would violate the exclusion principle. Also, there is no combination with $m_{l1} = 1$, $m_{s1} = -1/2$, $m_{l2} = 1$ and $m_{s2} = 1/2$ because this would differ from the first row combination $m_{l1} = 1$, $m_{s1} = 1/2$, $m_{l2} = 1$ and

$m_{s2} = -1/2$ solely by the interchange of electrons 1 and 2. Two rows that differ only by the exchange of two electrons correspond to the same Slater determinant, and as such, only one is included in the table.

Note that the highest value of M_L in the table is $M_L = 2$, which must correspond to a D term with $L = 2$. This M_L term occurs along with an $M_S = 0$ value, which implies $S = 0$. Thus there is a ^1D term corresponding to the five states

$$M_L = \quad 2 \quad 1 \quad 0 \quad -1 \quad -2$$
$$M_S = \quad 0 \quad 0 \quad 0 \quad \ \ 0 \quad \ \ 0$$

The highest M_S value in the table is $M_S = 1$ which indicates an $S = 1$ term. This occurs with $M_L = 1, 0, -1$ which indicates a P term. Hence we have a ^3P term that corresponds to the nine states

$$M_L = \quad 1 \quad 1 \quad \ \ 1 \quad 0 \quad 0 \quad \ \ 0 \quad -1 \quad -1 \quad -1$$
$$M_S = \quad 1 \quad 0 \quad -1 \quad 1 \quad 0 \quad -1 \quad \ \ 1 \quad \ \ 0 \quad -1$$

Deleting the above states from the table leaves the single state with $M_L = M_S = 0$, which corresponds to a ^1S term. Thus we see that a p^2 configuration of equivalent electrons gives rise to the terms ^1S, ^3P and ^1D. This is in contrast to the six terms ^1S, ^3S, ^1P, ^3P, ^1D and ^3D that arise from two nonequivalent electrons.

Suppose we have a configuration that contains both equivalent and nonequivalent electrons. We first find all terms that arise from each set separately, and then take all possible combinations of the resulting L and S values between the two sets. For example, suppose we have an sp^3 configuration. The s electron yields a ^2S term, and the three equivalent p electrons yield the terms ^2P, ^2D and ^4S (work it out or look it up). The terms with multiplicity 2 imply $S = 1/2$, and the term with multiplicity 4 implies $S = 3/2$. The ^2S term implies $L = 0$, so the possible total L values that result from combining the L values from each set are just the L values from the p electrons. Therefore, combining the $2S$ term with the $2P$ term yields $S = 0, 1$ and $L = 1$ so we have the terms ^1P and ^3P. Combining ^2S with ^2D yields ^1D and ^3D. And combining ^2S with ^4S we have $S = 1, 2$ which then yields the terms ^3S and ^5S. Thus the terms that arise from a sp^3 configuration are ^1P, ^3P, ^1D, ^3D, ^3S, ^5S.

As you might have expected, we can also define the **total electronic angular momentum J** of an atom as the vector sum of the total electronic orbital angular momentum and the total electronic spin angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S}\,.$$

The operator $\mathbf{J}$ commutes with the Hamiltonian (28), and hence we may also characterize an atomic state by the eigenvalue J defined by

$$\hat{J}^2\Psi = J(J+1)\hbar^2\Psi\,.$$

And as usual, the possible values of J are given by

$$|L + S| \leq J \leq L + S\,.$$

While we have seen that with the Hamiltonian (28), all states that belong to the same term have the same energy, once we include spin–orbit interactions, the value of J has a small effect on the energy levels. Thus states that belong to the same term but with different J values will have slightly different energies. The set of states that belong to the same term and also have the same J value are said to comprise an atomic **level**, and hence the different levels that belong to the same term have slightly different energies. Each level is comprised of $(2J+1)$ degenerate **states** because there are $2J + 1$ possible values of M_J, where $J_z \Psi = M_J \hbar \Psi$. To denote the level of a term, we add J as a subscript on the lower right of the term symbol:

$$^{2S+1}L_J.$$

To describe the multiplicity $2S + 1 = 1, 2, 3, 4, 5 \ldots$ we use the words **singlet**, **doublet**, **triplet**, **quartet**, **quintet** and so forth. Thus the level symbol $^3P_1$ would be described as a "triplet P one."

Example 7. Let us find the levels and corresponding degeneracies of a ^3P term. Clearly, a ^3P term has $L = 1$ and $S = 1$, so the possible J values are $J = 0, 1, 2$. This means that we have the levels $^3P_0$, $^3P_1$ and $^3P_2$. The level $^3P_0$ is nondegenerate, the level $^3P_1$ is 3-fold degenerate since $M_J = 0, \pm 1$, and the $^3P_2$ level is 5-fold degenerate because we have $M_J = 0, \pm 1, \pm 2$.

The total number of states for these three levels is $1 + 3 + 5 = 9$. This is in agreement with our earlier discussion that ignored spin–orbit coupling. There we showed that the term ^{2S+1}L had a degeneracy $(2L + 1)(2S + 1)$, and in the case of a ^3P term, this also yields a degeneracy $(3)(3) = 9$. Including the spin–orbit interaction has the effect of splitting these 9 degenerate states into three closely spaced levels, where one level has one state, another level is comprised of 3 states, and the third level is comprised of 5 states.

Example 8. A hydrogen atom has only a single electron so that $L = l$, $S = s = 1/2$, and hence $J = L \pm 1/2$ for $L > 0$, and $J = 1/2$ if $L = 0$. A given electron configuration gives rise to a single term, and this term is comprised of a single level if $L = 0$, and two levels if $L > 0$. The ground state configuration $1s$ gives the term ^2S which is comprised of the single 2-fold degenerate level $^2S_{1/2}$. For exactly the same reason, a $2s$ configuration gives the same 2-fold degenerate $^2S_{1/2}$ level. For a $2p$ configuration we again have a multiplicity of 2, but now $L = 1$ so that $J = 1/2, 3/2$ and we have the 2-fold degenerate level $^2P_{1/2}$ and the 4-fold degenerate level $^2P_{3/2}$. Thus there are $2 + 2 + 4 = 8$ states with $n = 2$.

To decide which of the terms that arise from a given electron configuration is lowest in energy, we use the empirical **Hund's rules**:

1. The term with largest S lies lowest in energy.

2. If there is more than one term with the largest S, then the term with largest S and largest L value lies lowest in energy.

These rules work very well for ground state configurations, but not as well for excited states. Also, remember that Hund's rules give only the state of lowest energy in the configuration, and should not be used to order higher states.