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$$[\hat{L}_i, \frac{\hat{p}_i}{2m}] = [\hat{L}_i, \frac{1}{2m} \sum_j p_j^2] =$$
Orbital Angular Momentum

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\[ [\hat{L}_i, \frac{\hat{p}_i \hat{p}}{2m}] = [\hat{L}_i, \frac{1}{2m} \sum_j p_j^2] = 0. \] (7.48)
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$$[\hat{L}_i, \hat{H}] = [\hat{L}_i, -\frac{\hbar^2}{2M} \nabla^2 + V(r)]$$
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$$[\hat{L}^2, \hat{H}] = 0.$$  \hspace{1cm} (7.50)
Orbital Angular Momentum

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\]

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[\hat{L}^2, \hat{H}] = 0 .
\]

(7.49)  
(7.50)

In other words, \( \hat{H}, \hat{L}_i \) and \( \hat{L}^2 \) all commute with one another.

This is an important and powerful result.
So, for any spherically symmetric potential $V(r)$, we have that

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In other words, $\hat{H}$, $\hat{L}_i$ and $\hat{L}^2$ all commute with one another.

**This is an important and powerful result.** Given any 3D quantum system, we can find a basis of simultaneous eigenfunctions of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$. 
We can translate the definitions of $\hat{L}_i$ to spherical polars. We have

$$x_1 = r \sin \theta \cos \phi, \quad x_2 = r \sin \theta \sin \phi, \quad x_3 = r \cos \theta. \quad (7.51)$$
Orbital Angular Momentum

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We thus obtain

\[ i\hbar (\cos \phi \cot \theta \frac{\partial}{\partial \phi} + \sin \phi \frac{\partial}{\partial \theta}) = -i\hbar (x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2}) \]
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We can also obtain

\[ \hat{L}^2 = \sum_i \hat{L}_i^2 = (\hat{L}_1 + i\hat{L}_2)(\hat{L}_1 - i\hat{L}_2) + i[\hat{L}_1, \hat{L}_2] + \hat{L}_3^2 \]
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Recall that $[\hat{L}^2, \hat{L}_3] = 0$. 
Recall that $[\hat{L}^2, \hat{L}_3] = 0$. We have

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We can thus seek simultaneous eigenfunctions of the form $Y(\theta) \exp(i m \phi)$,
Recall that $[\hat{L}^2, \hat{L}_3] = 0$. We have

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We can thus seek simultaneous eigenfunctions of the form $Y(\theta) \exp(i m \phi)$, since $\hat{L}_3 \exp(i m \phi) = \hbar m \exp(i m \phi)$. 
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We can thus seek simultaneous eigenfunctions of the form $Y(\theta) \exp(i m \phi)$, since $\hat{L}_3 \exp(i m \phi) = \hbar m \exp(i m \phi)$. As $\phi$ is defined modulo $2\pi$, we need $e^{i m (\phi + 2\pi)} = e^{i m \phi}$, so $e^{i 2m\pi} = 1$ and $m$ is an integer.
This leaves us with an eigenvalue equation for $\hat{L}^2$:
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\[-\hbar^2 \left( \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} \right) Y(\theta) = \lambda Y(\theta). \quad (7.59)\]
Orbital Angular Momentum

This leaves us with an eigenvalue equation for $\hat{L}^2$:

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From a physics perspective, the key fact about this equation is that we can show it has non-singular solutions if and only if $\lambda = \hbar^2 l(l + 1)$ for some integers $l \geq 0$. 


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From a physics perspective, the key fact about this equation is that we can show it has non-singular solutions if and only if $\lambda = \hbar^2 l(l+1)$ for some integers $l \geq 0$ and for $m$ in the range $-l \leq m \leq l$. 
The solutions are called the \textit{associated Legendre functions} $P_{l,m}(\theta)$. 
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Orbital Angular Momentum

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$$-\hbar^2 \frac{d}{dw} \left( (1 - w^2) \frac{dY}{dw} \right) - \left( \lambda - \frac{m^2}{1 - w^2} \right) Y = 0.$$  

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Orbital Angular Momentum

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For $m = 0$ and $\lambda = \hbar^2 l(l + 1)$ this is Legendre's differential equation for functions of degree $l$, which has solution $P_l(w)$. For general $m$ it's an associated Legendre differential equation. The associated Legendre functions can be obtained from the Legendre polynomials $P_l$ by

$$P_{l,m}(\theta) = (\sin \theta)^{|m|} \frac{d^{|m|}}{d(\cos \theta)^{|m|}} P_l(\cos \theta).$$  \hspace{1cm} (7.61)

(up to normalisation. Note that the solutions for -m are proportional to those for m, for given l.)
We thus have the overall solution given by the spherical harmonic with total angular momentum quantum number $l$ and $\hat{L}_3$ quantum number $m$: 
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Orbital Angular Momentum

We thus have the overall solution given by the spherical harmonic with total angular momentum quantum number \( l \) and \( \hat{L}_3 \) quantum number \( m \):

\[
Y_{l,m}(\theta, \phi) = P_{l,m}(\theta) \exp(im\phi),
\]

an eigenfunction of \( \hat{L}^2 \) and \( \hat{L}_3 \) with eigenvalues \( \hbar^2 l(l + 1) \) and \( \hbar m \) respectively.
We thus have the overall solution given by the spherical harmonic with total angular momentum quantum number $l$ and $\hat{L}_3$ quantum number $m$:

$$Y_{l,m}(\theta, \phi) = P_{l,m}(\theta) \exp(\text{i}m\phi),$$

an eigenfunction of $\hat{L}^2$ and $\hat{L}_3$ with eigenvalues $\hbar^2 l(l + 1)$ and $\hbar m$ respectively.

For plots of some spherical harmonics see e.g. mathworld.wolfram.com/SphericalHarmonic.html.
Solving the 3D Schrödinger equation for a spherically symmetric potential

The time-independent SE is

\[-\frac{\hbar^2}{2M} \nabla^2 \psi + V(r)\psi = E\psi.\]  \hspace{1cm} (7.62)
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Recall that in spherical polar coordinates

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$$\hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right).$$  \hfill (7.63)
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$$\hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right).$$  \hspace{1cm} (7.63)

So we have

$$-\hbar^2 \nabla^2 = -\hbar^2 \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \hat{L}^2.$$  \hspace{1cm} (7.64)
Solving the 3D Schrödinger equation for a spherically symmetric potential

We can thus rewrite the SE as

\[-\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{2Mr^2} \hat{L}^2 \right) \psi(r, \theta, \phi) + V(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi). \tag{7.65}\]
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If we separate variables, writing \( \psi(r, \theta, \phi) = \psi(r) Y_{l,m}(\theta, \phi) \), this gives
Solving the 3D Schrödinger equation for a spherically symmetric potential

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So, we have a standard 1D radial Schrödinger equation for \( \psi(r) \), with the modified potential \( V(r) + \frac{\hbar^2 l(l+1)}{2Mr^2} \).
Solving the 3D Schrödinger equation for a spherically symmetric potential

**Comment:** If the angular momentum \( l = 0 \) then also \( m = 0 \), and the function \( Y_{00}(\theta, \phi) \) is constant.
Solving the 3D Schrödinger equation for a spherically symmetric potential

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Conversely, since the $Y_{lm}$ for $l \neq 0$ are orthogonal to $Y_{00}$, all spherically symmetric states have zero angular momentum.
Solving the 3D Schrödinger equation for a spherically symmetric potential

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\[
\psi(\theta, \phi) = C
\]

Conversely, since the \( Y_{lm} \) for \( l \neq 0 \) are orthogonal to \( Y_{00} \), all spherically symmetric states have zero angular momentum.

This makes sense physically, since a state \( \psi \) with \( \langle L \rangle_\psi \neq 0 \) by definition has a nonzero vector associated with it, which breaks spherical symmetry.

\[
\langle L \rangle_\psi \neq 0
\]
The values of $E$ for which this equation is solvable clearly may depend on $l$ but not on $m$. 
Degeneracies

\[- \frac{\hbar^2}{2M} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \psi(r) + \left( \frac{\hbar^2}{2Mr^2} l(l + 1) + V(r) \right) \psi(r) = E \psi(r).\]

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The values of $E$ for which this equation is solvable clearly may depend on $l$ but not on $m$. As there are $(2l + 1)$ possible values of $m$, each energy level would have degeneracy $(2l + 1)$, assuming there are no further degeneracies.
Solving the 3D Schrödinger equation for a spherically symmetric potential

Given, 1D case: ground state of lowest energy are even parity. veilbein symmetric pot.  

**Theorem**

The ground state (i.e. lowest energy bound state) solution of the 3D Schrödinger equation for a spherically symmetric potential must have \( l = m = 0 \) and is thus spherically symmetric.
Solving the 3D Schrödinger equation for a spherically symmetric potential

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**Proof**  
The proof is by contradiction.
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Solving the 3D Schrödinger equation for a spherically symmetric potential

Now as $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$ are commuting hermitian operators, the space of wavefunctions is spanned by their simultaneous eigenstates.
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I.e., the eigenstates $\psi_i$ are all spherically symmetric solutions.
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I.e., the eigenstates $\psi_i$ are all spherically symmetric solutions. We can thus write $\psi(r) = \sum_i c_i \psi_i(r)$ for some constants $c_i$ such that $\sum_i |c_i|^2 = 1$. 
Solving the 3D Schrödinger equation for a spherically symmetric potential

\[ E = \int_{r=0}^{\infty} \psi^*(r) \left( -\frac{\hbar^2}{2M} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \right) \psi(r) \]
Solving the 3D Schrödinger equation for a spherically symmetric potential

\[ E = \int_{r=0}^{\infty} \psi^*(r) \left( -\frac{\hbar^2}{2M} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{\hbar^2}{2Mr^2} l(l + 1) + V(r) \right) \psi(r) \]  

(7.69)
Solving the 3D Schrödinger equation for a spherically symmetric potential

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\]

\[
= \int_{r=0}^{\infty} \psi^*(r) \left( -\frac{\hbar^2}{2M} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + V(r) \right) \psi(r) \right) \\
+ \int_{r=0}^{\infty} \psi^*(r) \left( \frac{\hbar^2}{2Mr^2} l(l + 1) \psi(r) \right) \tag{7.70}
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Solving the 3D Schrödinger equation for a spherically symmetric potential

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\[ > \int_{r=0}^{\infty} \psi^*(r) \left( -\frac{\hbar^2}{2M} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + V(r) \right) \right) \psi(r) \]  

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E > \int_{r=0}^{\infty} \psi^*(r) \left( -\frac{\hbar^2}{2M} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + V(r) \right) \right) \psi(r) \, dr
\]

\[
E = \int_{r=0}^{\infty} \sum_{i} c_i \psi^*_i(r) \left( -\frac{\hbar^2}{2M} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + V(r) \right) \right) \sum_{j} c_j \psi_j(r).
\]
Solving the 3D Schrödinger equation for a spherically symmetric potential

Now this last term is

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Since we have that \( E > \sum_i |c_i|^2 E_i \) and that \( \sum_i |c_i|^2 = 1 \),
Solving the 3D Schrödinger equation for a spherically symmetric potential

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Since we have that $E > \sum_i |c_i|^2 E_i$ and that $\sum_i |c_i|^2 = 1$, we must have that $E > E_i$ for at least one value of $i$. Hence $E$ is not the lowest energy eigenvalue, in contradiction to our original assumption.
The Hydrogen atom

We can now obtain the general bound state solution for particles in the potential $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$. 
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As we did in obtaining spherically symmetric solutions, we define the quantities

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a = \frac{e^2 M}{2\pi\epsilon_0 \hbar^2}, \quad b = \frac{\sqrt{-2MEN}}{\hbar}.
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We obtain from Eqn. (7.66) the equation

\[
\left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \psi(r) + \left( \frac{1}{r^2} l(l + 1) \right) + \frac{a}{r} \right) \psi(r) = b^2 \psi(r). \tag{7.73}
\]

\[
- \frac{\hbar^2}{2M} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \psi(r) + \left( \frac{\hbar^2}{2Mr^2} l(l + 1) + V(r) \right) \psi(r) = E \psi(r). \tag{7.66}
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As we saw in discussing Eqn. (7.26), we see that the ansatz \( \psi(r) \approx \exp(-br) \) means that the two asymptotically largest terms cancel.
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We can now obtain the general bound state solution for particles in the potential \( V(r) = -\frac{e^2}{4\pi \varepsilon_0 r} \).

As we did in obtaining spherically symmetric solutions, we define the quantities \( a = \frac{e^2 M}{2\pi \varepsilon_0 h^2} \), \( b = \frac{\sqrt{-2ME}}{h} \).

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\] (7.73)

As we saw in discussing Eqn. (7.26), we see that the ansatz \( \psi(r) \approx \exp(-br) \) means that the two asymptotically largest terms cancel. This again suggests trying an ansatz of the form \( \psi(r) = f(r) \exp(-br) \), for a power series \( f(r) \).
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\[ a_n \approx \frac{2b}{n} a_{n-1} \text{ for large } n, \]
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\[ \psi(r) \approx \exp(2br) \exp(-br) \approx \exp(br), \]
a divergent and unnormalisable wavefunction, which is physically unacceptable.
The power series must thus terminate, so we have $a = 2b(n + l)$, for some $n \geq 1$. 

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The power series must thus terminate, so we have \( a = 2b(n + l) \), for some \( n \geq 1 \). Thus \( b = \frac{a}{2N} \) for some \( N \geq l + 1 \), giving the same overall set of solutions for \( b \), and thus the same energy levels (i.e. the Bohr energy levels), as the spherically symmetric case with \( l = 0 \) we considered earlier:

\[
b = \frac{a}{lN} \quad n = 1, 2, 3, \ldots
\]
The power series must thus terminate, so we have \( a = 2b(n + l) \), for some \( n \geq 1 \). Thus \( b = \frac{a}{2N} \) for some \( N \geq l + 1 \), giving the same overall set of solutions for \( b \), and thus the same energy levels (i.e. the Bohr energy levels), as the spherically symmetric case with \( l = 0 \) we considered earlier:

\[
E = -\frac{Me^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{N^2}.
\]
Energy level degeneracies

Each value of $N$ is consistent with

$$I = 0, 1, \ldots (N - 1);$$
Energy level degeneracies

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$$l = 0, 1, \ldots (N - 1);$$  \hspace{1cm} (7.75)

each value of $l$ is consistent with

$$m = -l, -(l - 1), \ldots, l.$$
Energy level degeneracies

Each value of $N$ is consistent with

$$l = 0, 1, \ldots (N - 1); \quad (7.75)$$

each value of $l$ is consistent with

$$m = -l, -(l - 1), \ldots, l. \quad (7.76)$$

The total number of values of $(m, l)$ consistent with $N$ is thus

$$
\sum_{l=0}^{N-1} \sum_{m=-l}^{l} 1
$$
Energy level degeneracies

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The total number of values of $(m, l)$ consistent with $N$ is thus

$$\sum_{l=0}^{N-1} \sum_{m=-l}^{l} 1 = \sum_{l=0}^{N-1} (2l + 1) = 2\left(\frac{1}{2}N(N - 1)\right) + N = N^2.$$  \hspace{1cm} (7.77)
Energy level degeneracies

Each value of $N$ is consistent with

$$I = 0, 1, \ldots (N - 1);$$

(7.75)

each value of $I$ is consistent with

$$m = -I, -(I - 1), \ldots, I.$$  

(7.76)

The total number of values of $(m, I)$ consistent with $N$ is thus

$$\sum_{I=0}^{N-1} \sum_{m=-I}^{I} 1 = \sum_{I=0}^{N-1} (2I + 1) = 2\left(\frac{1}{2}N(N - 1)\right) + N = N^2.$$  

(7.77)

In fact, the true degeneracy of the $N$th energy level of the hydrogen atom in a full non-relativistic quantum mechanical treatment is $2N^2$: the extra factor of 2 arises from an intrinsically quantum mechanical degree of freedom, the electron spin, which has no direct classical analogue.
Towards the periodic table

We could try to generalize this discussion to atoms other than hydrogen. These have a nucleus with charge $+Ze$, orbited by $Z$ independent electrons, where the *atomic number* $Z$ is an integer greater than one.
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If we ignore this temporarily, we can obtain solutions of the form

$$\psi(x_1, \ldots, x_Z) = \psi_1(x_1) \ldots \psi_Z(x_Z),$$

(7.78)

where the $\psi_j$ are rescaled solutions for the hydrogen atom (the nucleus has charge $+Ze$ instead of $+e$).
Towards the periodic table

We could try to generalize this discussion to atoms other than hydrogen. These have a nucleus with charge \( +Ze \), orbited by \( Z \) independent electrons, where the \textit{atomic number} \( Z \) is an integer greater than one.

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If we ignore this temporarily, we can obtain solutions of the form

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\psi(x_1, \ldots, x_Z) = \psi_1(x_1) \cdots \psi_Z(x_Z),
\]

where the \( \psi_j \) are rescaled solutions for the hydrogen atom (the nucleus has charge \( +Ze \) instead of \(+e\)). The energy is just the sum

\[
E = \sum_{i=1}^{Z} E_i.
\]
Towards the periodic table

It turns out that for relatively small atoms this gives qualitatively the right form, with corrections arising from the electron-electron interactions that can be calculated using perturbation theory.
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So the lowest overall energy state is given by filling up the energy levels in order of increasing energy, starting with the lowest.
Towards the periodic table

Allowing for the twofold degeneracy arising from spin, as above, we have $2N^2$ states in the $N$th energy level.
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Towards the periodic table

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Towards the periodic table.

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"good" bomb will explode if photon hits trigger

"dod" bomb will not explode — the photon just reflects.

Your problem: you have a stack of good and dod bombs, and you don't know which is which. Want to identify some good bombs.
Towards the periodic table

Allowing for the twofold degeneracy arising from spin, as above, we have $2N^2$ states in the $N$th energy level. This gives us an atom with a full energy level with $Z = 2, 10 = 8 + 2, \ldots$ for $N = 1, 2, \ldots$; these are the elements helium, neon, \ldots. The elements with outer electrons in the 1st and 2nd energy levels fill out the corresponding first two rows of the periodic table. The analysis gets more complicated as atoms get larger, because electron-electron interactions become more important, and this qualitative picture is not adequate for the third and higher rows of the periodic table.