Orbital Angular Momentum

Now we have that $\hat{r} = \sqrt{\sum_j \hat{x}_j{}^2}$. We also have that $[\hat{L}_i, \sum_j \hat{x}_j{}^2] = 0$. One can show from this that $[\hat{L}_i, \hat{r}] = 0$.

$$[L_i, f(\hat{r})] = [L_i, \hat{r}] f'(\hat{r}) = 0$$

for any function f of r.

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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.

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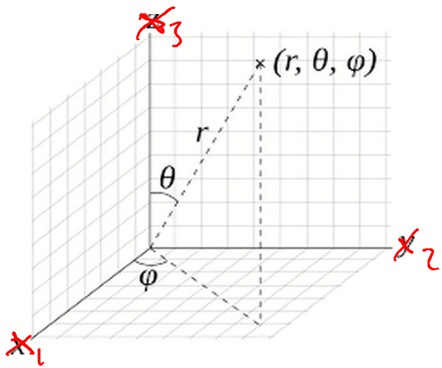
In other words, $\hat{H}, \hat{L}_i$ and $\hat{L}^2$ all commute with one another.

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 $\hat{L}_3$.

Orbital Angular Momentum

We can translate the definitions of $\hat{L}_i$ to spherical polars. We have

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



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We thus obtain

$$i\hbar(\cos\phi\cot\theta\frac{\partial}{\partial\phi}+\sin\phi\frac{\partial}{\partial\theta}) \quad = \quad -i\hbar(x_2\frac{\partial}{\partial x_3}-x_3\frac{\partial}{\partial x_2})$$

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Orbital Angular Momentum

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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&\qquad + i\hbar^2\frac{\partial}{\partial\phi} - \hbar^2\frac{\partial^2}{\partial\phi^2} \\
&= -\hbar^2(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}) \\
&= -\hbar^2(\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})\,. \qquad (7.57)
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We can thus seek simultaneous eigenfunctions of the form $Y(\theta)\exp(im\phi)$, since $\hat{L}_3 \exp(im\phi) = \hbar m \exp(im\phi)$. As ϕ is defined modulo 2π, we need $e^{im(\phi+2\pi)} = e^{im\phi}$, so $e^{i2m\pi} = 1$ and m is an integer.

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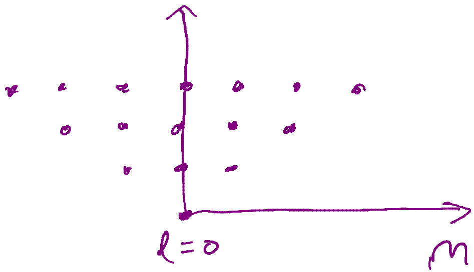

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For $m = 0$ and $\lambda = \hbar^2 l(l+1)$ this is Legendre's differential equation for functions of degree l, which has solution $P_l(w)$. For general m it's an associated Legendre differential equation. The associated Legendre functions can be obtained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

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

(up to normalisation. Note that the solutions for -m are proportional to those for m, for given l.)

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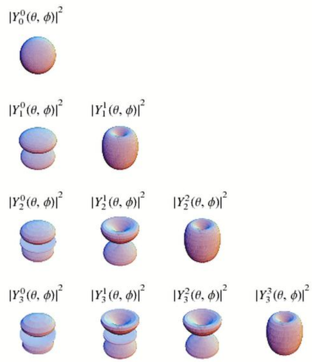
For plots of some spherical harmonics see e.g. mathworld.wolfram.com/SphericalHarmonic.html.



Solving the 3D Schrödinger equation for a spherically symmetric potential

The time-independent SE is

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Recall that in spherical polar coordinates

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\nabla^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \\
\hat{L}^2 &= -\hbar^2(\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})\,.
\end{aligned} \tag{7.63}$$

Solving the 3D Schrödinger equation for a spherically symmetric potential

The time-independent SE is

$$-\frac{\hbar^2}{2M}\nabla^2\psi + V(r)\psi = E\psi\,. \tag{7.62}$$

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\end{aligned} \tag{7.63}$$

So we have

$$-\hbar^2\nabla^2 = -\hbar^2(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) + \frac{1}{r^2}\hat{L}^2\,. \tag{7.64}$$

Solving the 3D Schrödinger equation for a spherically symmetric potential

We can thus rewrite the SE as

$$-\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\frac{1}{2Mr^2}\hat{L}^2)\psi(r,\theta,\phi)+V(r)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)\,. \tag{7.65}$$

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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

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$\int \psi(r)\, \psi'(r) = c c' \neq 0$.

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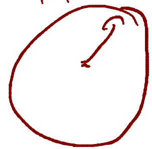

Conversely, since the Y_{lm} for $l \neq 0$ are orthogonal to Y_{00}, all spherically symmetric states have zero angular momentum.

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

$\langle \underline{L} \rangle_\psi$

Degeneracies

$$-\frac{\hbar^2}{2M}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)\psi(r)+\left(\frac{\hbar^2}{2Mr^2}l(l+1)\right)+V(r))\psi(r)=E\psi(r)\,. \tag{7.66}$$

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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

Cf. 1D case: ground state lowest energy state has even parity. reflection symmetric pot^{e}.

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.

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I.e., the eigenstates ψ_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

$$E = \int_{r=0}^{\infty} \psi^*(r)(-\frac{\hbar^2}{2M}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr})\psi(r)$$

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Solving the 3D Schrödinger equation for a spherically symmetric potential

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$= \int \sum_i c_i \psi_i^* \sum_j c_j E_j \psi_j$

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Solving the 3D Schrödinger equation for a spherically symmetric potential

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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. 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 divergent and unnormalisable wavefunction, which is physically unacceptable.

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This is what we found previously for $l = 0$

$b = \frac{a}{2N} \quad n = 1, 2, 3, \ldots$

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$$E = -\frac{Me^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{N^2}\,.$$

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In fact, the true degeneracy of the Nth 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.

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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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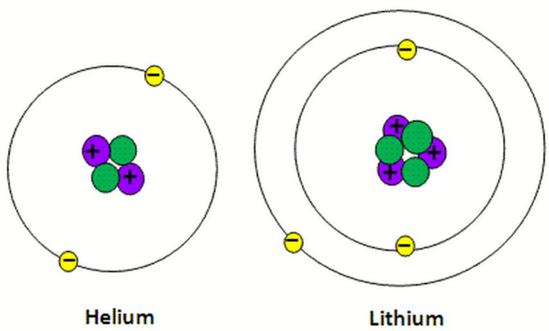

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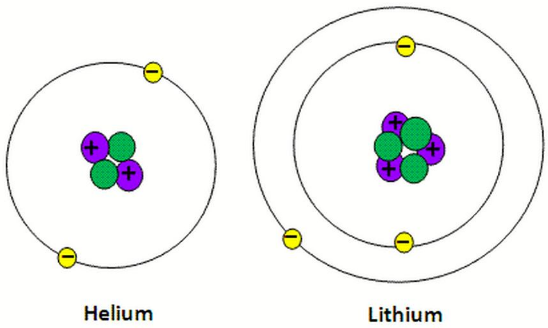

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where the ψ_j are rescaled solutions for the hydrogen atom (the nucleus has charge $+Ze$ instead of $+e$). The energy is just the sum

$$E = \sum_{i=1}^{Z} E_i \,. \tag{7.79}$$

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However, we also need to allow for the *Pauli exclusion principle*, which implies that no two electrons in the same atom can be in the same state.
So the lowest overall energy state is given by filling up the energy levels in order of increasing energy, starting with the lowest.

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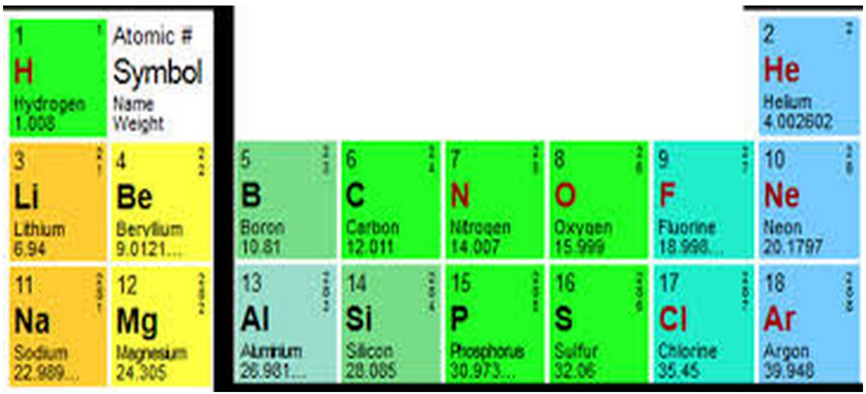

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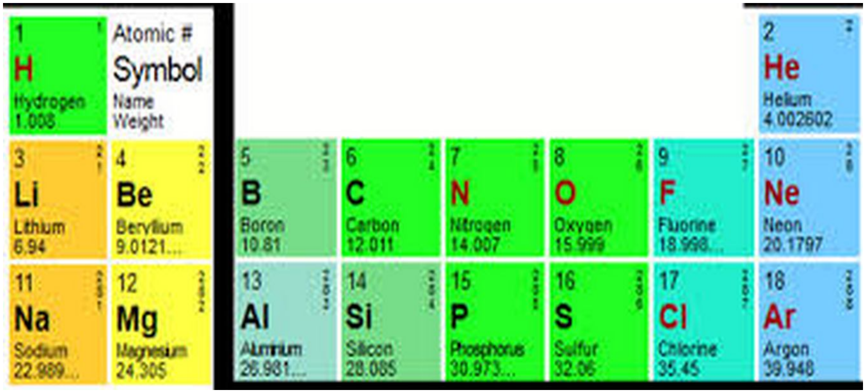

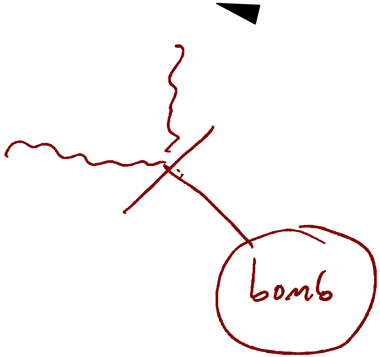

"good" bomb will explode if photon hits trigger

"dud" bomb will <u>not</u> explode — the photon just reflects.

Your problem: you have a stock of good + dud bombs, and you don't know which is which.
Want to identify some good bombs.

Towards the periodic table

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