Phys 506 Lecture 11: Cartesian hydrogen

1 Harmonic polynomials

We will solve hydrogen in Cartesian space without using angular momentum. To start, we must use the so-called harmonic polynomials, which are homogeneous polynomials in $\{r_x, r_y, r_z\}$ of degree l that satisfy $\nabla^2 P_h^l(r_x, r_y, r_z) = 0$. In terms of operators, they have two properties:

$$\left[\hat{r}\hat{p}_r, P_h^l(\hat{r}_x, \hat{r}_y, \hat{r}_z)\right] = -i\hbar l P_h^l(\hat{r}_x, \hat{r}_y, \hat{r}_z) \quad (1)$$

and

$$\sum_\alpha \left[\hat{p}_\alpha, \left[\hat{p}_\alpha, P_h^l(\hat{r}_x, \hat{r}_y, \hat{r}_z)\right]\right] = 0. \quad (2)$$

The first expression establishes that the harmonic polynomial is a homogeneous polynomial of order l. The second that the harmonic polynomial satisfies Laplace's equation, or $\nabla^2 P_h^l = 0$. Examples: $1, \hat{r}_x, \hat{r}_y, \hat{r}_z, \hat{r}_x^2 - \hat{r}_y^2, \hat{r}_x\hat{r}_y, \hat{r}_y\hat{r}_z, \hat{r}_z\hat{r}_x$, and $\hat{r}_x^2 + \hat{r}_y^2 - 2\hat{r}_z^2$. These are the s, p, and d spherical harmonics in a Cartesian basis. Note that the harmonic polynomials have definite l, but need not be eigenvectors of $\hat{L}_z$, and this makes them different from the $|l, m\rangle$ states. In particular,

$$\frac{1}{\hat{r}^l} p_h^l(\hat{r}_z, \hat{r}_y, \hat{r}_z)$$

is a function only of $\cos\hat{\theta}, \sin\hat{\theta}, \cos\hat{\phi}$ and $\sin\hat{\phi}$. This means it commutes with $\hat{p}_r$, which can be established directly by using property (1).

2 Cartesian factorization

The Cartesian factorization of $\hat{H}$ was discovered by Ioffe and coworkers in 1984, as part of the supersymmetric quantum mechanics craze ushered in by Ed Witten. Let's see how it works. The claim is that we can rewrite the Coulomb Hamiltonian in terms of the sum of three terms, each of the form of our conventional factorization. This looks like

$$\hat{H}(\lambda) = \sum_\alpha \frac{\hat{p}_\alpha^2}{2\mu} - \frac{e^2}{\lambda\hat{r}} = \sum_\alpha \hat{A}_\alpha^\dagger(\lambda)\hat{A}_\alpha(\lambda) + \tilde{E}_\lambda$$

with $\hat{A}_\alpha(\lambda) = \frac{1}{\sqrt{2\mu}}\left(\hat{p}_\alpha - \frac{i\hbar}{\lambda a_0}\frac{\hat{r}_\alpha}{\hat{r}}\right)$ and $\hat{E}_\lambda = -\frac{e^2}{2a_0\lambda^2}$. Note that the factor λ^2 in the denominator means the factorization holds for all λ, but the physical Hamiltonian corresponds to $\lambda = 1$.
Proof:

$$\hat{A}_\alpha^\dagger(\lambda)\hat{A}_\alpha(\lambda) = \frac{1}{2\mu}\left(\hat{p}_\alpha^2 - \frac{i\hbar}{\lambda a_0}\left[\hat{p}_\alpha, \frac{\hat{r}_\alpha}{\hat{r}}\right] + \frac{\hbar^2}{\lambda^2\alpha_0^2}\frac{\hat{r}_\alpha^2}{\hat{r}^2}\right) \text{ but } \left[\hat{p}_\alpha, \frac{\hat{r}_\alpha}{\hat{r}}\right] = -i\hbar\frac{1}{\hat{r}} + i\hbar\frac{\hat{r}_\alpha^2}{\hat{r}^3}$$

So

$$\hat{A}_\alpha^\dagger(\lambda)\hat{A}_\alpha(\lambda) = \frac{\hat{p}_\alpha^2}{2\mu} - \frac{\hbar^2}{2\mu a_0 \lambda}\frac{1}{\hat{r}} + \frac{\hbar^2}{2\mu a_0 \lambda}\frac{\hat{r}_\alpha^2}{\hat{r}^3} + \frac{\hbar^2}{2\mu a_0^2 \lambda^2}\frac{\hat{r}_\alpha^2}{\hat{r}^2}.$$

Now, sum over α and recall $\sum_\alpha \hat{r}_\alpha^2 = \hat{r}^2$, so

$$\textstyle\sum_\alpha \hat{A}_\alpha^\dagger(\lambda)\hat{A}_\alpha(\lambda) = \frac{\hat{p}_x^2}{2\mu} + \frac{\hat{p}_y^2}{2\mu} + \frac{\hat{p}_z^2}{2\mu} - \frac{3\hbar^2}{2\mu a_0 \lambda}\frac{1}{\hat{r}} + \frac{\hbar^2}{2\mu a_0 \lambda}\frac{1}{\hat{r}} + \frac{\hbar^2}{2\mu a_0^2 \lambda^2}.$$

Using $\frac{\hbar^2}{\mu a_0^2} = e^2$, we get

$$\frac{\hat{p}_x^2}{2\mu} + \frac{\hat{p}_y^2}{2\mu} + \frac{\hat{p}_z^2}{2\mu} - \frac{e^2}{\lambda \hat{r}} + \frac{e^2}{2a_0\lambda^2} \Rightarrow \tilde{E}_\lambda = -\frac{e^2}{2a_0\lambda^2}.$$

So we have established that

$$\hat{H}(\lambda) = \sum_\alpha \hat{A}_\alpha^\dagger(\lambda)\hat{A}_\alpha(\lambda) + \tilde{E}_\lambda.$$

This implies that the ground state satisfies $\hat{A}_\alpha(\lambda{=}1)\left|\psi_1\right\rangle = 0 \quad \text{for} \quad \alpha = x, y, z$, which can be rewritten as

$$\hat{p}_\alpha \left|\psi_1\right\rangle = \frac{i\hbar}{a_0}\frac{\hat{r}_\alpha}{\hat{r}}\left|\psi_1\right\rangle \quad \text{and} \quad E_{gs} = \tilde{E}_{\lambda=1} = -\frac{e^2}{2a_0}$$

As before we use ψ to denote the states of the original Hamiltonian, and because the physical one has $\lambda = 1$, we use the 1 subscript. Similarly, the ground states of the auxiliary Hamiltonians satisfy

$$\hat{A}_\alpha(\lambda)\left|\phi_\lambda\right\rangle = 0 \Rightarrow \hat{p}_\alpha\left|\phi_\lambda\right\rangle = \frac{i\hbar}{\lambda a_0}\frac{\hat{r}_\alpha}{\hat{r}}\left|\phi_\lambda\right\rangle \quad \text{and} \quad \tilde{E}_\lambda = -\frac{e^2}{2a_0\lambda^2}.$$

The full derivation of the Cartesian Hamiltonian approach is quite technical and we will just tell you some results, while some others will be homework problems.

3 Perpendicular kinetic energy

We start by defining the "perpendicular" kinetic energy via

$$\frac{1}{2\mu}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) = \frac{1}{2\mu}\hat{p}_r^2 + \hat{T}_\perp \Rightarrow \hat{T}_\perp = \frac{1}{2\mu}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 - \hat{p}_r^2\right).$$

This “perpendicular” kinetic energy should be equal to $\hat{L}^2/\hat{r}^2$, but we do not need that fact in our work (although it can be useful for intuition about how to proceed at times). One critical identity you will show on the HW is that

$$\hat{T}_\perp P_h^l\left(\hat{r}_x, \hat{r}_y, \hat{r}_z\right) \mid \phi_\lambda\rangle = \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2} P_h^l\left(\hat{r}_x, \hat{r}_y, \hat{r}_z\right)\left|\phi_\lambda\right\rangle.$$

As we said above, this implies $\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}$ annihilates $P_h^l\left(\hat{r}_x, \hat{r}_y, \hat{r}_z\right)\left|\phi_\lambda\right\rangle$ and that $P_h^l\left(\hat{r}_x, \hat{r}_y, \hat{r}_z\right) \mid \phi_\lambda\rangle$ has total angular momentum l. The latter comes from $\hat{T}_\perp = \frac{\hat{\mathbf{L}}^2}{2\mu\hat{r}^2}$ or $\hat{\mathbf{L}}^2 P_h^l\left(\hat{r}_x, \hat{r}_y, \hat{r}_z\right) \mid \phi_\lambda\rangle = \hbar^2 l\left(l+1\right) P_h^l\left(\hat{r}_x \hat{r}_y, \hat{r}_z\right)\left|\phi_\lambda\right\rangle$.

4 Intertwining

Intertwining is also complex and just sketched here, with more details in the homework, using the ladder operators we had before $\hat{B}_r(\lambda) = \frac{1}{\sqrt{2\mu}}\left(\hat{p}_r - i\hbar\left(\frac{1}{a_0\lambda} - \frac{\lambda}{\hat{r}}\right)\right)$ and the appropriate commutation relations. Then we have

$$\hat{B}_r^\dagger(\lambda)\hat{B}_r(\lambda) + \tilde{E}_\lambda = \frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2\lambda(\lambda+1)}{2\mu\hat{r}^2} - \frac{e^2}{\hat{r}}$$
$$\hat{B}_r(\lambda)\hat{B}_r^\dagger(\lambda) + \tilde{E}_{\lambda+1} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2(\lambda+1)(\lambda+2)}{2\mu\hat{r}^2} - \frac{e^2}{\hat{r}}.$$

This then implies that

$$\hat{H}(\lambda{=}1) = \hat{B}_r^\dagger(\lambda)\hat{B}_r(\lambda) + \hat{T}_\perp - \frac{\hbar^2\lambda(\lambda+1)}{2\mu\hat{r}^2} + \tilde{E}_\lambda$$
$$\hat{H}(\lambda{=}1) = \hat{B}_r(\lambda)\hat{B}_r^\dagger(\lambda) + \hat{T}_\perp - \frac{\hbar^2(\lambda+1)(\lambda+2)}{2\mu\hat{r}^2} + \tilde{E}_{\lambda+1}.$$

To set up intertwining, we compute

$$\left[\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}, \hat{B}_r^\dagger(\lambda)\right] = -\frac{2i\hbar}{\sqrt{2\mu}\hat{r}}\left[\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}\right].$$

Proof:

$$\left[\hat{T}_\perp - \frac{\hbar^2(l(l+1)}{2\mu\hat{r}^2}, \frac{1}{\sqrt{2\mu}}\left[\hat{p}_r + i\hbar\left(\frac{1}{\lambda a_0} - \frac{\lambda}{\hat{r}}\right)\right]\right] \quad \text{and} \quad \hat{T}_\perp = \frac{\hat{\mathbf{L}}^2}{2\mu\hat{r}^2} \quad \text{so}$$
$$\frac{1}{\sqrt{2\mu}}\frac{\hat{\mathbf{L}}^2}{2\mu}\left[\frac{1}{\hat{r}^2}, \hat{p}_r\right] - \frac{\hbar^2 l(l+1)}{2\mu}\frac{1}{\sqrt{2\mu},}\left[\frac{1}{\hat{r}^2}, \hat{p}_r\right]$$
$$= -\frac{2i\hbar}{\sqrt{2\mu}\hat{r}}\left(\frac{\hat{\mathbf{L}}^2}{2\mu\hat{r}^2} - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}\right) = -\frac{2i\hbar}{\sqrt{2\mu}\hat{r}}\left(\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}\right).$$

So $\left(\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}\right)\hat{B}_r^\dagger(\lambda) = \left(\hat{B}_r^\dagger(\lambda) - \frac{2i\hbar}{\sqrt{2\mu,\hat{r}}}\right)\left(\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}\right)$. This means we can move $\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu r^2}$ through $\hat{B}_r^\dagger$ with a shift being applied to $\hat{B}_r^\dagger$.

We will show that $|\psi_{nl}\rangle = \hat{B}_r^\dagger(l)\hat{B}_r^\dagger(l+1)\cdots\hat{B}_r^\dagger(n-2)r^{n-l-1}P_h^l\left(\hat{r}_x, \hat{r}_y, \hat{r}_z\right) \mid \phi_n\rangle$ is an eigenstate of the hydrogen Hamiltonian.

On the HW you will show intertwining:

$$\hat{H}(\lambda{=}1)\hat{B}_r^\dagger(l)\hat{B}_r^\dagger(l+1)\cdots\hat{B}_r^\dagger(n-2) = \hat{B}_r^\dagger(l)\cdots\hat{B}_r^\dagger(n-2)\left(\hat{H}(\lambda{=}1) + \frac{\hbar^2}{\mu\hat{r}^2}\sum_{j=1}^{n-l-1}(n-j)\right)$$
$$+\left\{\left(\hat{B}_r^\dagger(l) - \frac{2i\hbar}{\sqrt{r\mu}\hat{r}}\right)\left(\hat{B}_r^\dagger(l+1) - \frac{2i\hbar}{\sqrt{r\mu}\hat{r}}\right)\cdots\left(\hat{B}_r^\dagger(n-2) - \frac{2i\hbar}{\sqrt{2\mu}\hat{r}}\right)\right.$$
$$\left. - \hat{B}_r^\dagger(l)\cdots\hat{B}_r^\dagger(n-2)\right\}\left[\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}\right]$$

5 Energy eigenstate

To show our ansatz is an eigenstate, we recall that

$$\left(\hat{T}_\perp - \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2}\right)\hat{r}^{n-l-1}P_h^l\left(\hat{r}_x,\hat{r}_y,\hat{r}_z\right)\mid\phi_n\rangle = 0,$$

so that

$$\hat{H}(\lambda{=}1)\,|\psi_{nl}\rangle = \hat{B}_r^\dagger(l)\cdots\hat{B}_r^\dagger(n-2)\left[\hat{H}(\lambda{=}1) + \frac{\hbar^2}{\mu\hat{r}^2}\sum_{j=0}^{n-l-1}(n-j)\right]\hat{r}^{n-l-1}P_n^l(\hat{r}_x,\hat{r}_y,\hat{r}_z)|\phi_n\rangle.$$

We can move $\frac{P_h^l(\hat{r}_x,\hat{r}_y,\hat{r}_z)}{\hat{r}^l}$ to the left because it commutes with $\hat{p}_r$(after getting rid of $\hat{T}_\perp$). Also

$$\sum_{j=0}^{n-l-1}(n-1) = n(n-l-1) - \frac{1}{2}(n-1)(n-l-1) = (n-l-1)(n+l)\frac{1}{2}$$
$$= \left[n^2 - n - l(l+1)\right]\frac{1}{2}$$

We can write

$$\hat{H}(\lambda{=}1) + \frac{\hbar^2}{\mu\hat{r}^2}\sum_{j=0}^{n-l-1}(n-j) = \frac{\hat{p}_r^2}{2\mu} + \underbrace{\hat{T}_\perp - \frac{e^2}{\hat{r}} + \frac{\hbar^2}{\mu\hat{r}^2}n(n-1) - \frac{\hbar^2}{\mu\hat{r}^2}l(l+1)}_{\text{annihilate against } P_h^l(\hat{r}_x,\hat{r}_y,\hat{r}_z)}$$

So, we have that

$$\hat{H}(\lambda{=}1)\,|\psi_{nl}\rangle = \hat{B}_r^\dagger(l)\cdots\hat{B}_r^\dagger(n-2)\frac{P_h^l\left(\hat{r}_x,\hat{r}_y,\hat{r}_z\right)}{\hat{r}^l}\left[\frac{\hat{p}_r^2}{2\mu} - \frac{e^2}{\hat{r}} + \frac{\hbar^2}{\mu\hat{r}^2}n(n-1)\right]\hat{r}^{n-1}|\,\phi_n\rangle.$$

But

$$\begin{aligned}\hat{p}_r^2\hat{r}^{n-1} &= \hat{p}_r\left[\hat{p}_r,\hat{r}^{n-1}\right] + \hat{p}_r\hat{r}^{n-1}\hat{p}_r\\ &= -i\hbar(n-1)\hat{p}_r\hat{r}^{n-2} + \hat{p}_r\hat{r}^{n-1}\hat{p}_r\\ &= -i\hbar(n-1)\hat{r}^{n-2}\hat{p}_r - \hbar^2(n-1)(n-2)\hat{r}^{n-3} + \hat{r}^{n-1}\hat{p}_r^2 - i\hbar(n-1)\hat{r}^{n-2}\hat{p}_r\\ &= \hat{r}^{n-1}\left(\hat{p}_r^2 - 2i\hbar(n-1)\frac{1}{\hat{r}}\hat{p}_r - \hbar^2\frac{(n-1)(n-2)}{r^2}\right).\end{aligned}$$

So

$$\hat{H}(\lambda{=}1)\mid\psi_{nl}\rangle = \hat{B}_r^\dagger(l)\cdots\hat{B}_r^\dagger(n-2)\frac{P_h^l\left(\hat{r}_x,\hat{r}_y,\hat{r}_z\right)}{\hat{r}^l}\hat{r}^{n-1}$$
$$\left(\frac{\hat{p}_r^2}{2\mu} - \frac{e^2}{\hat{r}} - \frac{i\hbar(n-1)}{\mu}\frac{1}{\hat{r}}\underbrace{\hat{p}_r}_{i\hbar(\frac{1}{na_0}-\frac{1}{\hat{r}})} + \frac{\hbar^2}{2\mu\hat{r}^2}\underbrace{(n(n-1)-(n-1)(n-2))}_{2(n-1)}\right)|\phi_n\rangle\,,$$

because

$$\hat{p}_\alpha|\phi_n\rangle = \frac{i\hbar}{na_0}\frac{\hat{r}_\alpha}{\hat{r}}|\phi_n\rangle \Rightarrow \hat{p}_r|\phi_n\rangle = i\hbar\left(\frac{1}{na_0} - \frac{1}{\hat{r}}\right)|\phi_n\rangle.$$

Then we have that $\hat{H}(\lambda{=}1)|\phi_n\rangle$ becomes

$$= \hat{B}_r^\dagger(l)\cdots\hat{B}_r^\dagger(n-2)\frac{P_h^l\left(\hat{r}_x,\hat{r}_y\hat{r}_z\right)}{\hat{r}^l}\hat{r}^{n-1}\left(\frac{\hat{p}_r^2}{2\mu}-\frac{e^2}{\hat{r}}-\frac{\hbar^2}{\mu a_0}\frac{n-1}{n}\frac{1}{\hat{r}}-\underbrace{\frac{\hbar^2}{\mu\hat{r}^2}(n+1)+\frac{\hbar^2}{\mu\hat{r}^2}(n-1)}_{0}\right)|\phi_n\rangle$$

$$= \hat{B}_r^\dagger(l)\cdots\hat{B}_r^\dagger(n-2)P_h^l\left(\hat{r}_x,\hat{r}_y\hat{r}_z\right)\hat{r}^{n-1}\underbrace{\left(\frac{\hat{p}_r^2}{2\mu}-\frac{e^2}{n\hat{r}}\right)}_{\hat{H}(\lambda=n)}|\phi_n\rangle.$$

Hence, using the fact that $\hat{H}(\lambda{=}n)|\phi_n\rangle = \tilde{E}_n|\phi_n\rangle$, we find the final result that $\hat{H}(\lambda{=}1)\left|\psi_{nl}\right\rangle = \tilde{E}_n\left|\psi_{nl}\right\rangle$ ✓

Just like before, the string of $\hat{B}_r^\dagger(e)\cdots\hat{B}_r^\dagger(n-2)$ can get replaced by a Laguerre polynomial. I will do the algebra for you. We have that the normalized eigenfunction is

$$\left|\psi_{nl}\right\rangle = (-i)^{n-l-1}\left(\tfrac{na_0}{2}\right)^{n-1}\sqrt{\tfrac{(2n-1)!(n-l-1)!}{(n+l)!}}\tfrac{1}{\hat{r}^l}P_h^l\left(\hat{r}_x\hat{r}_y\hat{r}_z\right)\left(\tfrac{2\hat{r}}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\tfrac{2r}{na_0}\right)\left\langle x,y,z|\phi_n\right\rangle.$$

6 Position-space wavefunction

To get the wave function, we take the overlap with $\langle x,y,z|$ to find (operators are replaced by x,y,z)

$$\left\langle x,y,z \mid \psi_{nl}\right\rangle = \psi_{nl}(x,y,z) = (-i)^{n-l-1}\left(\frac{na_0}{2}\right)^{n-1}\sqrt{\frac{(2n-1)!(n-l-1)!}{(n+l)!}}\frac{P_h^l(x,y,z)}{r^l}$$
$$\times\left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)\left\langle x,y,z\,|\phi_n\right\rangle.$$

To obtain $\langle x,y,z \mid \phi_n\rangle$, we use the translation operator in spherical coordinates.

$$\langle x,y,z \mid \phi_n\rangle = \langle 0|e^{\frac{ir}{\hbar}(\hat{p}_r+\frac{i\hbar}{\hat{r}})}|\phi_n\rangle.$$

But,

$$\hat{p}_r\left|\phi_n\right\rangle = i\hbar\left(\frac{1}{na_0}-\frac{1}{\hat{r}}\right)\left|\phi_n\right\rangle$$

So

$$(\hat{p}_r+\frac{i\hbar}{\hat{r}})|\phi_n\rangle = \frac{i\hbar}{na_0}\left|\phi_n\right\rangle \quad \text{eigenvector!}$$

This implies that

$$\langle x,y,z|\phi_n\rangle = e^{-\frac{r}{na_0}}\langle 0|\phi_n\rangle.$$

which gives the position-space wave function, up to a normalization factor.

7 Momentum-space wavefunction

But what we really want is the momentum-space wave function

$$\tilde{\psi}\left(p_x,p_y,p_z\right) = \left\langle p_x,p_y,p_z \mid \psi_{nl}\right\rangle$$

Here, we are challenged, because $|p_x, p_y, p_z\rangle$ is not an eigenstate of $\hat{p}_r$. Doing the full calculation is technical and tough, but can be completed. Instead, we look first at how to get the $n=1, l=0$ case where we have $P_h^l(\hat{r}_x, \hat{r}_y, \hat{r}_z) = 1$.

$$\begin{aligned}\tilde{\psi}_{10}(p_x, p_y p_z) = \langle p_x, p_y, p_z \mid \psi_1\rangle &= \langle 0_p| e^{-\frac{i}{\hbar}(p_x\hat{r}_x + p_y\hat{r}_y + p_z\hat{r}_z)} |\psi_1\rangle \\ &= \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \frac{1}{n!}\langle 0_p| (p_x\hat{r}_x + p_y\hat{r}_y + p_z\hat{r}_z)^n |\psi_1\rangle .\end{aligned}$$

Look at $n=1$:

$$\langle 0_p \mid (p_x\hat{r}_x + p_y\hat{r}_y + p_z\hat{r}_z\rangle |\psi_1\rangle .$$

Recall that $\hat{p}_\alpha |\psi_1\rangle = \frac{i\hbar}{a_0}\frac{\hat{r}_\alpha}{\hat{r}}|\psi_1\rangle$, which implies that

$$\begin{aligned}&= \frac{a_0}{i\hbar}\langle 0_p| \hat{r}(p_x\hat{p}_x + p_y\hat{p}_y + p_z\hat{p}_z)|\psi_1\rangle \\ &= \frac{a_0}{i\hbar}\left(p_x\langle 0_p| [\hat{r}, \hat{p}_x]|\psi_1\rangle + p_y\langle 0_p| [\hat{r}, \hat{p}_y]|\psi_1\rangle + p_z\langle 0_p|[\hat{r}, \hat{p}_z]|\psi\rangle\right) \\ &= \frac{a_0}{i\hbar} i\hbar \sum_\alpha p_\alpha \langle 0_p| \underbrace{\frac{\hat{r}_\alpha}{\hat{r}}}_{\frac{a_0}{i\hbar}\hat{p}_\alpha} |\psi_1\rangle = \frac{a_0^2}{i\hbar}\sum_\alpha p_\alpha \langle 0_p| \hat{p}_\alpha |\phi_1\rangle = 0.\end{aligned}$$

So, it vanishes. We will find, in general, all odd powers vanish.

For the general case, consider

$$(p_x\hat{r}_x + p_y\hat{r}_y + p_z\hat{r}_z)^m = \sum_{\alpha_1}\sum_{\alpha_2}\cdots\sum_{\alpha_m} p_{\alpha_1}\hat{r}_{\alpha_1}p_{\alpha_2}\hat{r}_{\alpha_2}\cdots p_{\alpha_m}\hat{r}_{\alpha_m}$$

So

$$\langle 0_p| (p_x\hat{r}_x + p_y\hat{r}_y + p_z\hat{r}_z)^m \mid \psi_1\rangle = \sum_{\alpha_1}\cdots\sum_{\alpha_m} p_{\alpha_1}\cdots p_{\alpha_m}\langle 0_p| \hat{r}_{\alpha_1}\cdots\hat{r}_{\alpha_m}|\psi_1\rangle .$$

Just as before, we replace $\hat{r}_{\alpha_m}|\psi_1\rangle \to \frac{a_0}{i\hbar}\hat{r}\hat{p}_\alpha|\psi_1\rangle$ and recognize we have a commutator because $\hat{p}_\alpha \mid 0_p\rangle = 0$, so

$$\langle 0_p| (p_x\hat{r}_x + p_y\hat{r}_y + p_z\hat{r}_z)^m |\psi_1\rangle = \frac{a_0}{i\hbar}\sum_{\alpha_1\cdots\alpha_m} p_{\alpha_1}\cdots p_{\alpha_m}\langle 0_p| \left[\hat{r}_{\alpha_1}\cdots\hat{r}_{\alpha_{m-1}}\hat{r}, \hat{p}_{\alpha_m}\right]|\psi_1\rangle .$$

The commutator acts on $\hat{r}_{\alpha_j}$, and when $\alpha_j = \alpha_m$ it gives an $i\hbar$. Since we get the same result for each α_j from $j=1$ to $j=m-1$, we have $m-1$ terms. When $\hat{p}_{\alpha_m}$ is commuted with $\hat{r}$, it gives $i\hbar\frac{\hat{r}_\alpha}{\hat{r}}$, so we get

$$\begin{aligned}&= a_0 \cdot \mathbf{p}^2 \sum_{\alpha_1\cdots\alpha_{m-2}} p_{\alpha_2\cdots p_{\alpha_{m-2}}}(m-1)\langle 0_p| \hat{r}_{\alpha_1}\cdots\hat{r}_{\alpha_{m-2}}\hat{r}|\psi_1\rangle \\ &+ a_0 \sum_{\alpha_1\cdots\alpha_m} p_{\alpha_1}\cdots p_{\alpha_m}\langle 0_p| \hat{r}_{\alpha_1}\cdots\hat{r}_{\alpha_m}\frac{1}{\hat{r}}|\psi_1\rangle .\end{aligned}$$

In the first term, we write $\hat{r} = \sum_{\alpha_{m-1}}\frac{\hat{r}^2_{\alpha_{m-1}}}{\hat{r}} = \sum_{\alpha_{m-1}}\hat{r}_{\alpha_{m-1}}\frac{\hat{r}_{\alpha_{m-1}}}{\hat{r}}$ and replace by $\hat{p}_{\alpha_{m-1}}$ when acting on $|\psi_1\rangle$, so

$$\begin{aligned}&= \frac{a_0^2\mathbf{p}^2\sum_{\alpha_1\cdots\alpha_{m-1}}}{i\hbar}p_{\alpha_1}\cdots p_{\alpha_{m-2}}(m-1)\langle 0_p| [\hat{r}_{\alpha_1}\cdots\hat{r}_{\alpha_{m-1}}, \hat{p}_{\alpha_{m-1}}]|\psi_1\rangle \\ &\quad + \frac{a_0^2}{i\hbar}\sum_{\alpha_1\cdots\alpha_m} p_{\alpha_1}\cdots p_{\alpha_m}\langle 0_p| [\hat{r}_{\alpha_1}\cdots\hat{r}_{\alpha_{m-1}}, \hat{p}_{\alpha_m}]|\psi\rangle\end{aligned}$$

$$= a_0^2\mathbf{p}^2(m-1)(m-2+\overbrace{3}^{\text{from } \alpha_{m-1} \text{ case where there are 3 commutators}})\sum_{\alpha_1\cdots\alpha_{m-2}} p_{\alpha_1}\cdots p_{\alpha_{m-2}}\left\langle 0_p|\hat{r}_{\alpha_1}...\hat{r}_{\alpha_{m-2}} \mid \psi_1\right\rangle$$

$$+ a_0^2(m-1)\mathbf{p}^2 \sum_{\alpha_1\cdots\alpha_{m-2}} p_{\alpha_1}\cdots p_{\alpha_{m-2}}\left\langle 0_p|\hat{r}_{\alpha_1}\cdots\hat{r}_{\alpha_{m-2}}\,|\psi_1\right\rangle$$

So $\langle 0_p|\left(\sum_\alpha p_\alpha\hat{r}_\alpha\right)^m|\psi_1\rangle = (a_0p)^2\,(m-1)(m+2)\,\langle 0_p|\left(\sum_\alpha p_\alpha\hat{r}_\alpha\right)^{m-2}|\psi_1\rangle$.

This implies that all odd powers vanish, since we eventually hit $m=0$. Call $\langle 0_p|\left(\sum_\alpha p_\alpha\hat{r}_a\right)^m|\psi_1\rangle = N_m$. This then implies that

$$\begin{aligned} N_m &= (m-1)(m+2)(a_0p)^2N_{m-2} \\ &= (m-1)(m+2)(m-3)m\,(a_0p)^4\,N_{m-4} \\ &\vdots \\ &= m!\left(\frac{m}{2}+1\right)(a_0p)^m\,\langle 0_p\mid\psi_1\rangle\,. \end{aligned}$$

So, $\tilde{\psi}_{10}\left(p_{x_1},p_{y_1},p_z\right) = \sum_{n=0}^{\infty}\left(\frac{-i}{\hbar}\right)^{2n}\frac{1}{(2n)!}(2n)!(n+1)\,(a_0p)^{2n}\,\langle 0_p\mid\psi_1\rangle$

$$= \sum_{n=0}^{\infty}(-1)^n\left(\frac{a_0p}{\hbar}\right)^{2n}(n+1)\langle 0_p\mid\psi_1\rangle.$$

Recall that the geometric series is given by $\frac{1}{1+z} = \sum_{n=0}^{\infty}(-1)^nz^n$. Then,

$$\begin{aligned} \frac{\partial}{\partial z}\frac{1}{1+z} &= \frac{-1}{(1+z)^2} = \sum_{n=0}^{\infty}(-1)^n nz^{n-1} \\ &= -\sum_{n=0}^{\infty}(-1)^n\,(n+1)z^n \end{aligned}$$

This implies that

$$\tilde{\Psi}_{10}\left(p_x,p_yp_z\right) = \frac{1}{\left(1+\left(\frac{a_0p}{\hbar}\right)^2\right)^2}\underbrace{\langle 0_p\mid\psi_1\rangle}_{\text{normalization constant}=\frac{\sqrt{8}}{\pi}}\,.$$

8 What an atom really looks like

Why do we care? Because this can be directly measured!

When an e^-scatters off of H, the scattering is proportional to $|\psi_{1s}(\mathbf{p})|^2$ and the data agree perfectly with the calculation

This is called election momentum spectroscopy and was first measured in 1981. It in also called $(e,2e)$ spectroscopy because the "reaction" is $e+H\rightarrow 2e+H^+$, as the fast electron, strips an electron off of the hydrogen atom. We only see the $1s$ state in the scattering, because there is no way to populate other excited states enough that they last in the excited state for enough time that the experiment can be done.

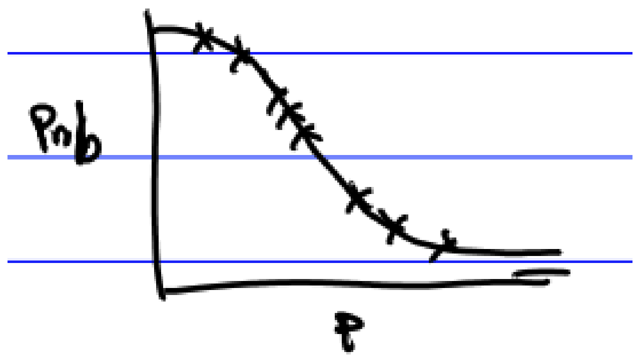

Figure 1: Sketch of what an e-2e experiment looks like. The probability distribution for an electron to be in a specific momentum eigenstate when we scatter off the 1s states of hydrogen looks like the square of a Lorentzian. It is high at $p = 0$, and then decays smoothly to zero for higher p. The experimentally measured data agree well with this result, which has no adjustable parameters.