

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:

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

$$2.) \quad \sum_d [\hat{p}_d, [P_h^l(\hat{r}_x, \hat{r}_y, \hat{r}_z)]] = 0$$

The first establishes it is a ^{homogeneous} polynomial of order l , the second that $\nabla^2 P_h^l = 0$.

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. Note that the harmonic polynomials have definite l , but need not be eigenvectors of \hat{L}_z . In particular $\frac{1}{r} P_h^l(\hat{r}_x, \hat{r}_y, \hat{r}_z)$ is a function only of $\cos\theta, \sin\theta, \cos\phi$ and $\sin\phi$.

The cartesian factorization of \hat{H} was discussed covered by Ittekk and co workers in 1984.

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

$$\text{with } \hat{A}_d(\lambda) = \frac{1}{\sqrt{2\mu}} \left(\hat{p}_d - \frac{i\hbar}{\lambda a_0} \frac{\hat{r}_d}{r} \right) \quad \tilde{E}_\lambda = -\frac{e^2}{2a_0 \lambda^2}$$

$$\text{Proof: } \hat{A}_d^+(\lambda) \hat{A}_d(\lambda) = \frac{1}{2\mu} \left(\hat{p}_d^2 - \frac{i\hbar}{\lambda a_0} [\hat{p}_d, \frac{\hat{r}_d}{r}] + \frac{\hbar^2}{\lambda^2 a_0^2} \frac{\hat{r}_d^2}{r^2} \right)$$

$$\text{but } [\hat{p}_d, \frac{\hat{r}_d}{r}] = -i\hbar \frac{1}{r} + i\hbar \frac{\hat{r}_d^2}{r^3}$$

$$\text{so } \hat{A}_d^+(\lambda) \hat{A}_d(\lambda) = \frac{\hat{p}_d^2}{2\mu} - \frac{\hbar^2}{2\mu a_0 \lambda} \frac{1}{r} + \frac{\hbar^2}{2\mu \lambda a_0} \frac{\hat{r}_d^2}{r^3} + \frac{\hbar^2}{2\mu \lambda^2 a_0^2} \frac{\hat{r}_d^2}{r^2}$$

Now, sum over d and recall $\sum_d \hat{r}_d^2 = \hat{r}^2$, so

$$\sum_d \hat{A}_d^+(\lambda) \hat{A}_d(\lambda) = \frac{\hat{p}_x^2}{2\mu} + \frac{\hat{p}_y^2}{2\mu} + \frac{\hat{p}_z^2}{2\mu} - \frac{3\hbar^2}{2\mu a_0 \lambda} \frac{1}{r} + \frac{\hbar^2}{2\mu \lambda a_0} \frac{1}{r} + \frac{\hbar^2}{2\mu \lambda^2 a_0^2}$$

$$\text{Using } \frac{\hbar^2}{\mu a_0} = e^2, \text{ we get } \frac{\hat{p}_x^2}{2\mu} + \frac{\hat{p}_y^2}{2\mu} + \frac{\hat{p}_z^2}{2\mu} - \frac{e^2}{\lambda r} + \frac{e^2}{2a_0 \lambda^2} \Rightarrow \tilde{E}_\lambda = -\frac{e^2}{2a_0 \lambda^2}$$

So we have established that

$$\hat{H}(\lambda) = \sum_{\alpha} \hat{A}_{\alpha}^{\dagger}(\lambda) \hat{A}_{\alpha}(\lambda) + \tilde{E}_{\lambda} \quad (2)$$

\Rightarrow ground state satisfies $\hat{A}_{\alpha}(\lambda=1) |\psi_0\rangle = 0 \quad \alpha=x,y,z$

$$\Rightarrow \hat{p}_{\alpha} |\psi_0\rangle = i\hbar \frac{\hat{r}_{\alpha}}{a_0} |\psi_0\rangle \quad E_{gs} = \tilde{E}_{\lambda=1} = -\frac{e^2}{2a_0}$$

The ground states of the auxiliary Hamiltonians satisfy

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

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.

We start by defining the "perpendicular" kinetic energy via $\frac{1}{2\mu}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) = \frac{1}{2\mu} \hat{p}_r^2 + \hat{T}_{\perp} \Rightarrow \hat{T}_{\perp} = \frac{1}{2\mu} (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 - \hat{p}_r^2)$

One critical identity you will show on the HW is that

$$\hat{T}_{\perp} P_n^{\ell}(\hat{r}_x, \hat{r}_y, \hat{r}_z) |\phi_{\lambda}\rangle = \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2} P_n^{\ell}(\hat{r}_x, \hat{r}_y, \hat{r}_z) |\phi_{\lambda}\rangle$$

This implies $\hat{T}_{\perp} - \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2}$ annihilates $P_n^{\ell}(\hat{r}_x, \hat{r}_y, \hat{r}_z) |\phi_{\lambda}\rangle$

and that $P_n^{\ell}(\hat{r}_x, \hat{r}_y, \hat{r}_z) |\phi_{\lambda}\rangle$ has ^{total} angular momentum ℓ .

The latter comes from $\hat{T}_{\perp} = \hat{L}^2 - \hat{L}_r^2$ or $\hat{L}^2 P_n^{\ell}(\hat{r}_x, \hat{r}_y, \hat{r}_z) |\phi_{\lambda}\rangle = \hbar^2 \ell(\ell+1) P_n^{\ell}(\hat{r}_x, \hat{r}_y, \hat{r}_z) |\phi_{\lambda}\rangle$

Interesting is also complex and just sketched here, with more details in the homework.

Using the commutation relations we had before $\hat{B}_r(\lambda) = \frac{1}{2\mu} (\hat{p}_r - i\hbar(\frac{1}{a_0} - \frac{1}{\lambda}))$

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

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

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

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

To set up intertwining, we compute

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

Proof:

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

$$\begin{aligned} & \frac{1}{\sqrt{2\mu}} \frac{\hbar^2}{2\mu} \left[\frac{1}{\hat{r}^2}, \hat{p}_r \right] - \frac{\hbar^2 \ell(\ell+1)}{2\mu} \frac{1}{\sqrt{2\mu}} \left[\frac{1}{\hat{r}^2}, \hat{p}_r \right] \\ &= -\frac{2i\hbar}{\sqrt{2\mu} \hat{r}} \left(\frac{\hbar^2}{2\mu \hat{r}^2} - \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2} \right) = -\frac{2i\hbar}{\sqrt{2\mu} \hat{r}} \left(\hat{T}_\perp - \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2} \right) \end{aligned}$$

$$\text{so } \left(\hat{T}_\perp - \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2} \right) \hat{B}_r^\dagger(\lambda) = \left(\hat{B}_r^\dagger(\lambda) - \frac{2i\hbar}{\sqrt{2\mu} \hat{r}} \right) \left(\hat{T}_\perp - \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2} \right)$$

This means we can move $\hat{T}_\perp - \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2}$ through \hat{B}_r^\dagger

with a shift being applied to \hat{B}_r^\dagger .

We will show that $|\psi_n\rangle = \hat{B}_r^\dagger(\ell) \hat{B}_r^\dagger(\ell+1) \dots \hat{B}_r^\dagger(n-2) \hat{r}^{n-2} P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z) |\phi_n\rangle$ is an eigenstate. on the HW you will show intertwining:

$$\begin{aligned} \hat{H}(\lambda=1) \hat{B}_r^\dagger(\ell) \hat{B}_r^\dagger(\ell+1) \dots \hat{B}_r^\dagger(n-2) &= \hat{B}_r^\dagger(\ell) \dots \hat{B}_r^\dagger(n-2) \left(\hat{H}(\lambda=1) + \frac{\hbar^2}{\mu \hat{r}^2} \sum_{j=0}^{n-1} (n-j) \right) \\ &+ \left\{ \left(\hat{B}_r^\dagger(\ell) - \frac{2i\hbar}{\sqrt{2\mu} \hat{r}} \right) \left(\hat{B}_r^\dagger(\ell+1) - \frac{2i\hbar}{\sqrt{2\mu} \hat{r}} \right) \dots \left(\hat{B}_r^\dagger(n-2) - \frac{2i\hbar}{\sqrt{2\mu} \hat{r}} \right) \right. \\ &\left. - \hat{B}_r^\dagger(\ell) \dots \hat{B}_r^\dagger(n-2) \right\} \left[\hat{T}_\perp - \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2} \right] \end{aligned}$$

To show our ansatz is an eigenstate, we recall that

$$\left(\hat{T}_\perp - \frac{\hbar^2 \ell(\ell+1)}{2\mu \hat{r}^2} \right) \hat{r}^{n-2} P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z) |\phi_n\rangle = 0 \quad \text{so that}$$

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

We can move $\frac{P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z)}{\hat{r}^\ell}$ to the left because it commutes with \hat{B}_r^\dagger (after getting rid of \hat{T}_\perp)

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

$$\hat{H}(\lambda=1) + \frac{\hbar^2}{\mu \hat{r}^2} \sum_{j=0}^{n-1} (n-j) = \frac{\hat{p}_r^2}{2\mu} + \hat{T}_\perp - \frac{e^2}{\hat{r}} + \frac{\hbar^2}{\mu \hat{r}^2} n(n-1) - \frac{\hbar^2}{\mu \hat{r}^2} \ell(\ell+1)$$

(annihilate against $P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z)$)

$$\text{so } \hat{H}(\lambda=1) |\psi_n\rangle = \hat{B}_r^\dagger(\ell) \dots \hat{B}_r^\dagger(n-2) \frac{P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z)}{\hat{r}^\ell} \left[\frac{\hat{p}_r^2}{2\mu} - \frac{e^2}{\hat{r}} + \frac{\hbar^2}{\mu \hat{r}^2} n(n-1) \right] \hat{r}^{n-1} |\phi_n\rangle$$

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

$$\begin{aligned}
 \text{So } \hat{H}(\lambda=1)|\psi_{n\ell}\rangle &= \hat{B}_r^\dagger(\ell) \dots \hat{B}_r^\dagger(n-2) \frac{P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z)}{\hat{r}^\ell} \hat{r}^{n-1} \\
 &\quad \left(\frac{\hat{P}_r^2}{2\mu} - \frac{e^2}{\hat{r}} - \frac{i\hbar(n-1)}{\mu} \frac{1}{\hat{r}} \hat{P}_r + \frac{\hbar^2}{2\mu\hat{r}^2} (n(n-1) - (n-1)(n-1)) \right) |\psi_n\rangle \\
 \hat{P}_r |\psi_n\rangle &= i\hbar \frac{\hat{r}_z}{na_0} \frac{1}{\hat{r}} |\psi_n\rangle \Rightarrow \hat{P}_r |\psi_n\rangle = i\hbar \left(\frac{1}{na_0} - \frac{1}{\hat{r}} \right) |\psi_n\rangle \quad \left[i\hbar \left(\frac{1}{na_0} - \frac{1}{\hat{r}} \right) \right] \uparrow z(n-1) \\
 &= \hat{B}_r^\dagger(\ell) \dots \hat{B}_r^\dagger(n-2) \frac{P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z)}{\hat{r}^\ell} \hat{r}^{n-1} \left(\frac{\hat{P}_r^2}{2\mu} - \frac{e^2}{\hat{r}} - \frac{\hbar^2}{2\mu\hat{r}^2} \frac{n-1}{n} \frac{1}{\hat{r}} - \frac{\hbar^2}{2\mu\hat{r}^2} (n-1) + \frac{\hbar^2}{2\mu\hat{r}^2} (n-1) \right) |\psi_n\rangle \\
 &= \hat{B}_r^\dagger(\ell) \dots \hat{B}_r^\dagger(n-2) P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z) \hat{r}^{n-1} \left(\frac{\hat{P}_r^2}{2\mu} - \frac{e^2}{\hat{r}} \right) |\psi_n\rangle \\
 &\quad \uparrow \hat{H}(\lambda=n) \quad \hat{H}(\lambda=n)|\psi_n\rangle = \tilde{E}_n |\psi_n\rangle
 \end{aligned}$$

$$\text{So } \hat{H}|\psi_{n\ell}\rangle = \tilde{E}_n |\psi_{n\ell}\rangle \quad \checkmark$$

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

$$\begin{aligned}
 |\psi_{n\ell}\rangle &= (-i)^{n-\ell-1} \left(\frac{na_0}{z} \right)^{n\ell} \sqrt{\frac{(2n-1)!(n-\ell-1)!}{(n+\ell)!}} \frac{1}{\hat{r}^\ell} P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z) \\
 &\quad \left(\frac{z\hat{r}}{na_0} \right)^\ell L_{n-\ell-1}^{2\ell} \left(\frac{z\hat{r}}{na_0} \right) |\psi_n\rangle
 \end{aligned}$$

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

$$\begin{aligned}
 \langle x, y, z | \psi_{n\ell}\rangle &= \psi_{n\ell}(x, y, z) = (-i)^{n-\ell-1} \left(\frac{na_0}{z} \right)^{n\ell} \sqrt{\frac{(2n-1)!(n-\ell-1)!}{(n+\ell)!}} \frac{P_n^\ell(x, y, z)}{r^\ell} \\
 &\quad \left(\frac{zr}{na_0} \right)^\ell L_{n-\ell-1}^{2\ell} \left(\frac{zr}{na_0} \right) \langle x, y, z | \psi_n\rangle
 \end{aligned}$$

to obtain $\langle x, y, z | \psi_n\rangle$ we use the translation operator in spherical coordinates

$$\langle x, y, z | \psi_n\rangle = \langle 0 | e^{\frac{i\hat{r}}{\hbar} (\hat{P}_r + \frac{i\hbar}{\hat{r}})} | \psi_n\rangle$$

$$\text{But } \hat{P}_r |\psi_n\rangle = i\hbar \left(\frac{1}{na_0} - \frac{1}{\hat{r}} \right) |\psi_n\rangle$$

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

$$\Rightarrow \langle x, y, z | \psi_n\rangle = e^{-\frac{z}{na_0}}$$

which gives the position-space wave function.

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

$$\tilde{\Psi}(P_x, P_y, P_z) = \langle P_x, P_y, P_z | \psi_{n\ell}\rangle$$

here, we are challenged, because $\langle P_x, P_y, P_z |$ 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 $n=1, \ell=0$ case. $P_n^\ell(\hat{r}_x, \hat{r}_y, \hat{r}_z) = 1$.

$$\tilde{\Psi}_{10}(P_x, P_y, P_z) = \langle P_x, P_y, P_z | \Psi_1 \rangle$$

(5)

$$= \langle 0_p | e^{-\frac{i}{\hbar}(P_x \hat{r}_x + P_y \hat{r}_y + P_z \hat{r}_z)} | \Psi_1 \rangle$$

$$= \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \frac{1}{n!} \langle 0_p | (P_x \hat{r}_x + P_y \hat{r}_y + P_z \hat{r}_z)^n | \Psi_1 \rangle$$

Look at $n=1$:

$$\langle 0_p | P_x \hat{r}_x + P_y \hat{r}_y + P_z \hat{r}_z | \Psi_1 \rangle$$

$$\text{Recall } \hat{P}_d | \Psi_1 \rangle = \frac{i\hbar}{a_0} \frac{\hat{r}_d}{\tilde{r}} | \Psi_1 \rangle \Rightarrow$$

$$= \frac{a_0}{i\hbar} \langle 0_p | \hat{r} (P_x \hat{P}_x + P_y \hat{P}_y + P_z \hat{P}_z) | \Psi_1 \rangle$$

$$= \frac{a_0}{i\hbar} \left(P_x \langle 0_p | [\hat{r}, \hat{P}_x] | \Psi_1 \rangle + P_y \langle 0_p | [\hat{r}, \hat{P}_y] | \Psi_1 \rangle + P_z \langle 0_p | [\hat{r}, \hat{P}_z] | \Psi_1 \rangle \right)$$

$$= \frac{a_0}{i\hbar} i\hbar \sum_d P_d \langle 0_p | \frac{\hat{r}_d}{\tilde{r}} | \Psi_1 \rangle = \frac{a_0^2}{i\hbar} \sum_d P_d \langle 0_p | \hat{P}_d | \Psi_1 \rangle = 0$$

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

For the general case, consider

$$(P_x \hat{r}_x + P_y \hat{r}_y + P_z \hat{r}_z)^m = \sum_{d_1} \sum_{d_2} \dots \sum_{d_m} P_{d_1} \hat{r}_{d_1} P_{d_2} \hat{r}_{d_2} \dots P_{d_m} \hat{r}_{d_m}$$

$$\text{so } \langle 0_p | (P_x \hat{r}_x + P_y \hat{r}_y + P_z \hat{r}_z)^m | \Psi_1 \rangle = \sum_{d_1} \dots \sum_{d_m} P_{d_1} \dots P_{d_m} \langle 0_p | \hat{r}_{d_1} \dots \hat{r}_{d_m} | \Psi_1 \rangle$$

just as before, replace $\hat{r}_{d_m} | \Psi_1 \rangle \rightarrow \frac{a_0}{i\hbar} \hat{r} \hat{P}_{d_m} | \Psi_1 \rangle$ and recognize

we have a commutator because $\hat{P}_{d_m} | 0_p \rangle = 0$ so

$$\langle 0_p | (P_x \hat{r}_x + P_y \hat{r}_y + P_z \hat{r}_z)^m | \Psi_1 \rangle = \frac{a_0}{i\hbar} \sum_{d_1, \dots, d_m} P_{d_1} \dots P_{d_m} \langle 0_p | [\hat{r}_{d_1}, \dots, \hat{r}_{d_{m-1}}, \hat{r}, \hat{P}_{d_m}] | \Psi_1 \rangle$$

the commutator acts on \hat{r}_{d_j} when $d_j = d_m$ and gives an $i\hbar$. since

we get the same result for each d_j from $j=1$ to $j=m$, we have $m-1$ terms. When \hat{P}_{d_m} commutes with \hat{r} it gives $i\hbar \frac{\hat{r}_{d_m}}{\tilde{r}}$, so

we get

$$= a_0 \cdot \bar{P}^2 \sum_{d_1, \dots, d_{m-1}} P_{d_1} \dots P_{d_{m-1}} (m-1) \langle 0_p | \hat{r}_{d_1} \dots \hat{r}_{d_{m-1}} \hat{r} | \Psi_1 \rangle$$

$$+ a_0 \sum_{d_1, \dots, d_m} P_{d_1} \dots P_{d_m} \langle 0_p | \hat{r}_{d_1} \dots \hat{r}_{d_m} \frac{1}{\tilde{r}} | \Psi_1 \rangle$$

in the first term, write $\hat{r} = \sum_{d_{m-1}} \frac{\hat{r}_{d_{m-1}}}{\tilde{r}} = \sum_{d_{m-1}} \hat{r}_{d_{m-1}} \frac{\hat{r}_{d_{m-1}}}{\tilde{r}}$

and replace by $\hat{P}_{d_{m-1}}$ when acting on $|\Psi_1\rangle$ so

$$= \frac{a_0^2}{i\hbar} \bar{P}^2 \sum_{d_1, \dots, d_{m-1}} P_{d_1} \dots P_{d_{m-1}} (m-1) \langle 0_p | [\hat{r}_{d_1}, \dots, \hat{r}_{d_{m-1}}, \hat{P}_{d_{m-1}}] | \Psi_1 \rangle$$

$$+ \frac{a_0^3}{i\hbar} \sum_{d_1, \dots, d_m} P_{d_1} \dots P_{d_m} \langle 0_p | [\hat{r}_{d_1}, \dots, \hat{r}_{d_{m-1}}, \hat{P}_{d_m}] | \Psi_1 \rangle$$

← From dirac case where there are 3 commutators

$$= a_0^2 \vec{p}^2 (m-1)(m-2+3) \sum_{\alpha_1 \dots \alpha_{m-2}} p_{\alpha_1} \dots p_{\alpha_{m-2}} \langle 0_p | \hat{r}_{\alpha_1} \dots \hat{r}_{\alpha_{m-2}} | \psi_i \rangle$$

$$+ a_0^2 (m-1) \vec{p}^2 \sum_{\alpha_1 \dots \alpha_{m-2}} p_{\alpha_1} \dots p_{\alpha_{m-2}} \langle 0_p | \hat{r}_{\alpha_1} \dots \hat{r}_{\alpha_{m-2}} | \psi_i \rangle$$

so $\langle 0_p | (\sum_{\alpha} p_{\alpha} \hat{r}_{\alpha})^m | \psi_i \rangle = (a_0 p)^2 (m-1)(m+2) \langle 0_p | (\sum_{\alpha} p_{\alpha} \hat{r}_{\alpha})^{m-2} | \psi_i \rangle$

⇒ all odd vanish, since we eventually hit $m=0$

call $\langle 0_p | (\sum_{\alpha} p_{\alpha} \hat{r}_{\alpha})^m | \psi_i \rangle = \mu_m$

⇒ $\mu_m = (m-1)(m+2) (a_0 p)^2 \mu_{m-2}$

$= (m-1)(m+2)(m-3)m (a_0 p)^4 \mu_{m-4}$

⋮

$= m! \binom{m}{2} (a_0 p)^m \langle 0_p | \psi_i \rangle$

so $\check{\Psi}_{10}(p_x, p_y, p_z) = \sum_{n=0}^{\infty} \left(\frac{-i}{\hbar}\right)^{2n} \frac{1}{(2n)!} (2n)! (n!) (a_0 p)^{2n} \langle 0_p | \psi_i \rangle$

$$= \sum_{n=0}^{\infty} (-1)^n \left(\frac{a_0 p}{\hbar}\right)^{2n} (n!)$$

recall geometric series $\frac{1}{1+z} = \sum_{n=0}^{\infty} (-1)^n z^n$

$$\frac{\partial}{\partial z} \frac{1}{1+z} = \frac{-1}{(1+z)^2} = \sum_{n=0}^{\infty} (-1)^n n z^{n-1}$$

$$= - \sum_{n=0}^{\infty} (-1)^n (n+1) z^n$$

⇒ $\check{\Psi}_{10}(p_x, p_y, p_z) = \frac{1}{(1 + (\frac{a_0 p}{\hbar})^2)^2} \langle 0_p | \psi_i \rangle$

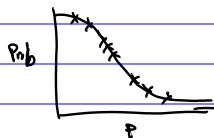
↑ normalization
constant. = $\frac{\sqrt{8}}{\pi}$

Why do we care? Because this can be measured

When an e^- scatters off of H,

the scattering is prop to $|\psi_{10}(\vec{p})|^2$

The data agree perfectly with the calculation



This is called electron momentum spectroscopy and was first measured in 1981.

It is also called $(e, 2e)$ spectroscopy because the "reaction" is $e + H \rightarrow 2e + H^+$

We only see the 1s, because there's no way to populate other excited states enough that they last in the excited state for enough time that the expt. can be done