Quantum Mechanics II

H-Atom Details

Spinless (Bohr) Model—A Reminder; Relativistic Corrections; Magnetic Corrections

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H-Atom

Spinless (Bohr) Model

Extra!

- The Schrödinger equation is

$$i\hbar\,\frac{\partial}{\partial t}\,\Psi(\vec{r},t) = H\,\Psi(\vec{r},t), \qquad H = \Big[-\frac{\hbar^2}{2m_e}\vec{\nabla}^2 + V(r)\Big]$$

- In spherical coordinates,

$$\vec{\nabla}^2(\cdots) = \frac{1}{r^2}\Big(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\cdots\Big) - \frac{1}{r^2}L^2(\cdots)$$

- Use $\boxed{L^2 Y_\ell^m(\theta,\phi) = \ell(\ell{+}1)\,Y_\ell^m(\theta,\phi)}$
- …to expand

$$\Psi_{n,\ell,m}(\vec{r},t) = e^{-i\omega_{n,\ell,m}t}\,R_{n,\ell}(r)\,Y_\ell^m(\theta,\phi), \qquad \omega_{n,\ell,m} := \frac{E_{n,\ell,m}}{\hbar}$$

- Also, since $\dfrac{1}{r^2}\Big(\dfrac{\partial}{\partial r}r^2\dfrac{\partial}{\partial r}\cdots\Big) \equiv \dfrac{1}{r}\Big(\dfrac{\partial^2}{\partial r^2}r\cdots\Big)$ write $R_{n,\ell}(r) = \dfrac{u_{n,\ell}(r)}{r}$
- we have:

$$-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2 u_{n,\ell}}{\mathrm{d}r^2} + \Big[\underset{\text{Coulomb}}{V(r)} + \underset{\text{Centrifugal}}{\frac{\hbar^2}{2m_e}\frac{\ell(\ell{+}1)}{r^2}}\Big]u_{n,\ell} = E_{n,\ell}\,u_{n,\ell}.$$

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$$-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2u_{n,\ell}}{\mathrm{d}r^2}+\Big[V(r)+\frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\Big]u_{n,\ell}=E_{n,\ell}\,u_{n,\ell}.$$

Spinless (Bohr) Model

Extra!

- The Coulomb potential:

$$V(r)=-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}=-\frac{\alpha_e\hbar c}{r},\qquad \alpha_e:=\frac{e^2}{4\pi\epsilon_0\hbar c}\sim{}^1/_{137}$$

- The solutions:

$\sim{}^1/_{18{,}769}$

characteristic energy: 511 keV

$$E_n=-\frac{1}{2}\boxed{\alpha_e^2}\boxed{m_ec^2}\frac{1}{n^2},\qquad n=1,2,3\ldots$$

$$\Psi_{n,\ell,m}(\vec{r},t)=\sqrt{\Big(\frac{2}{n\,a_0}\Big)^3\frac{(n-\ell-1)!}{2n[(n+1)!]^3}}\,e^{-r/(na_0)}\Big(\frac{2r}{na_0}\Big)^{\ell}L^{2\ell+1}_{n-\ell-1}\Big(\frac{2r}{na_0}\Big)\,Y^m_\ell(\theta,\phi)$$

$$a_0:=\frac{4\pi\epsilon_0\hbar^2}{m_ee^2}=0.529\times10^{-10}\,\mathrm{m}\qquad\text{is the Bohr radius}$$

- Degeneracy (for each $n = 1, 2, 3,\ldots$):

$$\ell=0,1,2\ldots(n-1),\qquad |m|\leqslant\ell,\ m\in\mathbb{Z},\qquad s=\pm\tfrac{1}{2}$$

$$\sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell}2=2\sum_{\ell=0}^{n-1}(2\ell+1)=2\,n^2$$

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$$-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2 u_{n,\ell}}{\mathrm{d}r^2} + \Big[V(r) + \frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\Big]u_{n,\ell} = E_{n,\ell}\,u_{n,\ell}.$$

$$E_n = -\frac{1}{2}\alpha_e^2\, m_e c^2\,\frac{1}{n^2}$$

Spinless (Bohr) Model

Extra!

- Energy independent of m (eigenvalue of L_3)
  - implies "indifference" to orientation of the L_3-axis
  - *i.e.*, rotational symmetry; $SO(3)$
- But, energy is also independent of ℓ!
  - This implies a larger symmetry.
  - Laplace-Runge-Lenz vector: for $V(r) = -\frac{\varkappa}{r}$, $\quad \vec{A} := \vec{p}\times\vec{L} - m_e\,\frac{\varkappa}{r}\,\vec{r}.$
  - …in classical physics. In quantum physics,

$$L_i := \frac{1}{\hbar}(\vec{r}\times\vec{p})_i = -i\,\varepsilon_{ij}{}^k\,x^j\frac{\partial}{\partial x^k}$$

$$A_j = \frac{1}{\sqrt{2m_e H}}\Big[\frac{\hbar}{2i}\varepsilon_j{}^{kl}\Big(\frac{\partial}{\partial x^k}L_l + L_l\frac{\partial}{\partial x^k}\Big) - \frac{m_e\,\varkappa}{\hbar}\,\hat{\mathrm{e}}_j\Big]$$

$$[L_j, L_k] = i\varepsilon_{jk}{}^l L_l, \quad [L_j, A_k] = -i\varepsilon_{jk}{}^l A_l, \quad [A_j, A_k] = \pm i\varepsilon_{jk}{}^l L_l, \;\text{ for }\; \Big\{\begin{smallmatrix}E<0,\\ E>0;\end{smallmatrix}$$

  - Rotations vary $m \in [-\ell, +\ell]$, while A-transformations varies $\ell \in [0, n-1]$.
  - Corrections will "break" this big symmetry, $SO(4)$ for bound states.

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$$-\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2u_{n,\ell}}{\mathrm{d}r^2}+\Big[V(r)+\frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\Big]u_{n,\ell}=E_{n,\ell}\,u_{n,\ell}$$

$$\alpha_e := \frac{e^2}{4\pi\epsilon_0\hbar c} \qquad E_n = -\frac{1}{2}\alpha_e^2\, m_e c^2\,\frac{1}{n^2}$$

Relativistic Corrections

Extra!

- A. Sommerfeld (1915) made Bohr’s model relativistic:

$$E_{n,k} = m_e c^2\left\{1+\Big[\frac{\alpha_e}{n-k+\sqrt{k^2-Z^2\alpha_e^2}}\Big]^2\right\}^{-1/2}$$

- where $n = 1, 2, 3\dots$ (size), $k = 1, 2\dots, n$ (ellipticity).
- Expand in α_e and obtain:

$$E_{n,k} = m_e c^2 + E_n - \frac{\alpha_e^2 Z^2}{4n^2}|E_n|\Big(\frac{4n}{k}-3\Big)+\dots$$

- $m_e c^2$ drops out in energy differences = line spectra energies.
- Corrections ($\alpha_e^2 \sim {}^1/_{18,769}$)× $|E_n|$ dubbed “fine structure.”
- This must be recovered by a consistent treatment of the Schrödinger equation, including effects that were omitted in the first approximation.

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Relativistic Corrections

$$E_{n,k} = m_e c^2 + E_n - \frac{\alpha_e^2 Z^2}{4n^2}|E_n|\left(\frac{4n}{k} - 3\right) + \dots$$

$$\alpha_e := \frac{e^2}{4\pi\epsilon_0\hbar c} \qquad E_n = -\frac{1}{2}\alpha_e^2\, m_e c^2\, \frac{1}{n^2}$$

Extra!

- Kinetic energy, relativistically:

$$T_{\text{rel}} = m_e c^2\left[\sqrt{1+(\vec{p}/m_e c)^2} - 1\right] = m_e c^2 \sum_{k=1}^{\infty} \binom{1/2}{k}\left(\frac{\vec{p}^2}{m_e^2 c^2}\right)^k$$

$$\approx \frac{\vec{p}^2}{2m_e} - \frac{(\vec{p}^2)^2}{8m_e^3 c^2} + \frac{(\vec{p}^2)^3}{16 m_e^5 c^4} - \dots$$

Ouch!

- Relativistic correction perturbation Hamiltonian terms:

$$H'_{\text{rel}} := -\frac{\hbar^4}{8m_e^3 c^2}(\vec{\nabla}^2)^2, \qquad H''_{\text{rel}} := +\frac{\hbar^6}{16 m_e^5 c^4}(\vec{\nabla}^2)^3,$$

$$E_n^{(1,r_1)} = \langle n|H'_{\text{rel}}|n\rangle \qquad \text{use} \quad \vec{\nabla}^2 = \frac{2m_e}{\hbar^2}\left[V(r) - H\right]$$

$$H'_{\text{rel}} = -\frac{1}{2m_e c^2}\left[V(r) - H\right]^2 = -\frac{1}{2m_e c^2}\left[V^2 - HV - VH + H^2\right],$$

$$E_n^{(1,r_1)} = \langle n,\ell,m,m_s|H'_{\text{rel}}|n,\ell,m,m_s\rangle = -\frac{1}{2m_e c^2}\left[\langle V^2\rangle - 2E_n^{(0)}\langle V\rangle + (E_n^{(0)})^2\right]$$

$$= -\alpha_e^4\, m_e c^2\, \frac{1}{4n^4}\left[\frac{2n}{(\ell+\frac{1}{2})} - \frac{3}{2}\right]$$

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Relativistic Corrections

Extra!

- For future reference:

$$\left\{\begin{aligned}\langle r^2\rangle &= n^4 a_0^{\,2}\Big[1+\tfrac{3}{2}\big(1-\tfrac{\ell(\ell+1)-\frac{1}{3}}{n^2}\big)\Big],\\ \langle r\rangle &= n^2 a_0\Big[1+\tfrac{1}{2}\big(1-\tfrac{\ell(\ell+1)}{n^2}\big)\Big],\\ \langle r^{-1}\rangle &= \frac{1}{n^2\,a_0},\\ \langle r^{-2}\rangle &= \frac{1}{(\ell+\frac{1}{2})n^3\,a_0^{\,2}},\\ \langle r^{-3}\rangle &= \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)n^3\,a_0^{\,3}}.\end{aligned}\right.$$

rotationally symmetric $SO(3)$ →

← Laplace-Runge-Lenz-symmetric $SO(4)$

Every ~1/r perturbation breaks the $SO(4)$ symmetry

- Clearly, there must be more to it than just

$$E_n^{(1,r_1)} = -\frac{1}{2}\alpha_e^4\, m_e c^2\,\frac{1}{4n^4}\Big[\frac{4n}{(\ell+\frac{1}{2})}-3\Big]$$

ought to be an integer

- What are we missing?
- Neither $E^{(1)}[H'']$ nor $E^{(2)}[H']$: both are $O(\alpha_e^6)$.

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Magnetic Corrections

Extra!

- Both e^- and p^+ have magnetic dipole moments

$$\vec{\mu}_e = -g_e \mu_B \vec{S}_e, \qquad \mu_B := \frac{e}{2m_e}, \qquad g_e = 2.002\,319\,304\,361\,1(46) \approx 2$$

$$\vec{\mu}_p = +g_p \mu_N \vec{S}_p, \qquad \mu_N := \frac{e}{2m_p}, \qquad g_p = 2.7928$$

- …and the mutual orbiting produces a magnetic field
  - Careful: e^- orbits about p^+ and creates a current and so a magnetic field

$$\vec{B} = \frac{\mu_0 I}{2R} \quad \Rightarrow \quad \vec{\mu} = -\frac{e}{2m_e}\vec{L} \qquad \text{with which } \mu_p \text{ interacts, but not } \mu_e$$

  - “Viewed” from the e^- frame, it’s p^+ that orbits around the e^-
  - at a speed calculated by Lorentz-boosting, moment-by-moment
  - which results in ½ of the magnetic field, with which μ_e interacts
- We thus have three magnetic interaction terms

$$-\vec{\mu}_e \cdot (\tfrac{1}{2}\vec{B}), \quad -\vec{\mu}_p \cdot \vec{B}, \quad -\frac{\mu_0}{4\pi}\Big[\Big(3(\vec{\mu}_e\cdot\hat{r})(\vec{\mu}_p\cdot\hat{r}) - \vec{\mu}_e\cdot\vec{\mu}_p\Big)\frac{1}{r^3} + \frac{8\pi}{3}\vec{\mu}_e\cdot\vec{\mu}_p\,\delta^3(\vec{r}\,)\Big]$$

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Magnetic Corrections

Extra!

- The three Hamiltonian perturbations are:

$$H_{S_eO} = -\Big(\frac{g_e(-e)}{2m_e}\hbar\vec{S}_e\Big)\cdot\Big(\tfrac{1}{2}\frac{e}{4\pi\epsilon_0 m_e r^3}\hbar\vec{L}\Big) \approx \frac{e^2}{4\pi\epsilon_0}\,\frac{\hbar^2}{2m_e^2c^2}\,\frac{1}{r^3}\,\vec{L}\cdot\vec{S}_e,$$

$$H_{S_pO} = \frac{g_p\,e^2}{4\pi\epsilon_0}\,\frac{\hbar^2}{m_e m_p c^2}\,\frac{1}{r^3}\,\vec{L}\cdot\vec{S}_p,$$

$g_e \approx 2\,(= 2.002\,319\ldots)$

$$H_{S_eS_p} \approx \frac{g_p\,e^2}{4\pi\epsilon_0}\,\frac{\hbar^2}{m_e m_p c^2}\Big[\Big(3(\vec{S}_e\cdot\hat{r})(\vec{S}_p\cdot\hat{r}) - \vec{S}_e\cdot\vec{S}_p\Big)\frac{1}{r^3} + \frac{8\pi}{3}\vec{S}_e\cdot\vec{S}_p\,\delta^3(\vec{r}\,)\Big]$$

- They all have the same powers of e, $\hbar$ and c as well as r
  - But the latter two are suppressed by $(m_e/m_p \approx {}^{1}/_{1{,}836})$!!
  - Thus: $$\langle H_{S_eO}\rangle = \frac{e^2}{4\pi\epsilon_0}\,\frac{\hbar^2}{2m_e^2c^2}\Big\langle\frac{1}{r^3}\,\vec{L}\cdot\vec{S}_e\Big\rangle \sim \frac{\alpha_e\hbar^3}{2m_e^2c}\cdot\frac{1}{a_0{}^3} = \frac{\alpha_e^4 m_e c^2}{2}$$
  - …which is of the same order as $E^{(1)}[H']$
  - and so must be included—regardless of Sommerfeld’s result.

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$$\langle H_{S_eO}\rangle = \frac{e^2}{4\pi\epsilon_0}\frac{\hbar^2}{2m_e^2c^2}\left\langle \frac{1}{r^3}\vec{L}\cdot\vec{S}_e\right\rangle$$

Magnetic Corrections

Extra!

$$\langle r^{-3}\rangle = \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)n^3\,a_0{}^3}$$

- To *compute* this, recall:

$$\vec{J} = \vec{L}+\vec{S} \quad\Rightarrow\quad \vec{J}^2 = \vec{L}^2+\vec{S}^2+2\vec{L}\cdot\vec{S} \quad\Rightarrow\quad \vec{L}\cdot\vec{S} = \tfrac{1}{2}\big(\vec{J}^2-\vec{L}^2-\vec{S}^2\big)$$

  - where $s(s+1) = ¾$ and $j = \ell \pm ½$
- The 1st order spin-orbital correction is therefore

$$E_n^{(1,SO)} = \alpha_e^4 m_e c^2 \frac{j(j+1)-\ell(\ell+1)-\frac{3}{4}}{\boxed{4n^3}\boxed{\ell(\ell+\frac{1}{2})(\ell+1)}} = \alpha_e^4 m_e c^3 \frac{1}{4n^3}\begin{cases} \dfrac{1}{(\ell+1)(\ell+\frac{1}{2})} \\ -\dfrac{1}{\ell(\ell+\frac{1}{2})} \end{cases}$$

- and adds to the relativistic correction:

$$E_n^{(1)} = -\alpha_e^4 m_e c^3 \frac{1}{4n^4}\begin{cases} \dfrac{2n}{\ell+\frac{1}{2}}-\dfrac{3}{2}-\dfrac{n}{(\ell+1)(\ell+\frac{1}{2})} = \dfrac{2n(\ell+1)-n}{(\ell+1)(\ell+\frac{1}{2})}-\dfrac{3}{2} \\ \dfrac{2n}{\ell+1}-\dfrac{3}{2}+\dfrac{n}{\ell(\ell+\frac{1}{2})} = \dfrac{2n\ell+n}{\ell(\ell+\frac{1}{2})}-\dfrac{3}{2} \end{cases}$$

H-Atom

$$\langle H_{S_eO}\rangle = \frac{e^2}{4\pi\epsilon_0}\frac{\hbar^2}{2m_e^2c^2}\left\langle \frac{1}{r^3}\,\vec{L}\cdot\vec{S}_e\right\rangle$$

Magnetic Corrections

Extra!

$$\langle r^{-3}\rangle = \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)n^3\,a_0^{\;3}}$$

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  - where $s(s+1) = ¾$ and $j = \ell \pm ½$

- The 1st order spin-orbital correction is therefore

$$E_n^{(1,SO)} = \alpha_e^4 m_e c^2 \frac{j(j+1)-\ell(\ell+1)-\frac{3}{4}}{4n^3\boxed{\ell(\ell+\frac{1}{2})(\ell+1)}} = \alpha_e^4 m_e c^3 \frac{1}{4n^3}\begin{cases} \dfrac{1}{(\ell+1)(\ell+\frac{1}{2})} \\ -\dfrac{1}{\ell(\ell+\frac{1}{2})} \end{cases}$$

- and adds to the relativistic correction:

$$E_n^{(1)} = -\alpha_e^4 m_e c^3 \frac{1}{4n^4}\begin{cases} \dfrac{2n}{\ell+\frac{1}{2}}-\dfrac{3}{2}-\dfrac{n}{(\ell+1)(\ell+\frac{1}{2})} = \dfrac{2n(\ell+\frac{1}{2})}{(\ell+1)(\ell+\frac{1}{2})}-\dfrac{3}{2} \\ \dfrac{2n}{\ell+1}-\dfrac{3}{2}+\dfrac{n}{\ell(\ell+\frac{1}{2})} = \dfrac{2n(\ell+\frac{1}{2})}{\ell(\ell+\frac{1}{2})}-\dfrac{3}{2} \end{cases}$$

$$= -\alpha_e^4\, m_e c^2\, \frac{1}{4n^4}\Big[\frac{2n}{(j+\frac{1}{2})}-\frac{3}{2}\Big], \qquad \begin{cases} \boxed{\begin{aligned} j &= \ell + ½, \\ j &= \ell - ½; \end{aligned}} \end{cases}$$

- This recovers Sommerfeld's 1st order term **×2** degeneracy!

H-Atom

$$E_{n,\ell} = -\frac{1}{2}\alpha_e^2\, m_e c^2 \frac{1}{n^2}\Big\{1 + \frac{\alpha_e^2}{4n^2}\Big[\frac{4n}{(j+\frac{1}{2})} - 3\Big] + \dots\Big\}$$
$$j = \ell \pm \tfrac{1}{2}$$

"Fine Structure" Corrections

Extra!

- The "fine structure" ($\alpha_e^2 \approx {}^1\!/_{18,769}$) corrections to energy
  - 1st order relativistic correction to KE (in Coulomb potential)
  - plus the "spin-orbital" magnetic interaction
  - calculated to the first order in perturbation theory
- equal the 1st order correction from Sommerfeld's formula
  - "plus" the spin-½ degeneracy
  - In 1915, Sommerfeld knew not of "spin" [Uhlenbeck+Goudsmit, 1925]
  - but relativity unites the electromagnetic field
  - and so "connects" the Coulomb potential with the magnetic interactions
- The expansion

$$T_{\text{rel}} = m_e c^2 \sum_{k=1}^{\infty} \binom{1/2}{k} \Big(\frac{\vec{p}^{\,2}}{m_e^2 c^2}\Big)^k$$

  - guarantees even p-powers, and so an even α_e-power expansion
  - much as is Sommerfeld's. × 2 for spin. But, there *is* more…

Quantum Mechanics II

Are you ready?

Mid-Term!

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