QM with Atomic Physics

By Downs, Finn, Steidle, Ume, & Yao

Formalism

symbols	meaning
$\Psi(x,t)$	Probability function of position and time, defines the probability of a particle occupying a position at a given time
Ψ^*	The complex conjugate (replace *i* with *–i)*
$\int_{-\infty}^{\infty} \Psi^*(x,t)\,\Psi(x,t)dx = 1$ $\int_{-\infty}^{\infty} \lvert\Psi(x,t)\rvert^2 dx = 1$	Normalization: the probability of finding a particle that exists somewhere, across all possible somewheres, is 1. Ψ may need to be normalized. Ψ goes to 0 at positive & negative infinity.
$\hat{A}$	An operator: a "rule" that acts on a function, in QM it acts on Ψ ex. $\frac{d}{dx}, 2x$
$\langle A \rangle$ $\int_{-\infty}^{\infty} \Psi^*(x,t)\hat{A}\Psi(x,t)dx = \langle A \rangle$	Expected value of A

If a function f(x) operated on by operator returns c*f(x), then f(x) is an eigenfunction of that operator, with eigenvalue c.

Math	English
$\int_{-\infty}^{\infty} f(x)^* \left(\hat{A}g(x)\right) dx = \int_{-\infty}^{\infty} \left(\hat{A}f(x)\right)^* g(x) dx$	Definition of a Hermitian operator
$\int_{-\infty}^{\infty} f(x)^* g(x) dx = 0$	Eigenfunctions corresponding to different eigenvalues are orthogonal.
$\hat{x} = x$ $\hat{p} = -i\hbar \frac{\partial}{\partial x}$	Position and momentum operators All other physical observable operators can be derived from these, except for spin.
$c_n = \int_{-\infty}^{\infty} f_n(x)^* \, \Psi(x,t) dx$	Cn is the probability coefficient of the function being in a specific state
$\langle A \rangle = \sum_k \lambda_k \lvert c_k \rvert^2$	The expectation value of A can be calculated if the eigenvalues and coefficients are known

Dirac delta notation

- aka bra(c)ket notation
- $|B>$ is "B ket"
- $<B|$ is "bra A"
- $\langle a|b\rangle := \langle b|a\rangle^*$
- "A dagger", which is the complex conjugate of the operator A
- If $\langle a|\hat{A}b\rangle := \langle \hat{A}^\dagger b|a\rangle^*$ is true, then A is Hermitian
- $\langle f|g\rangle := \int_{-\infty}^{\infty} f(x)^* g(x) dx$

Schrodinger equation

Equation	Explanation
$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t) = E_n\Psi(x,t)$	Schrodinger equation, all solutions are energy states
$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}(x)$	The Hamiltonian operator
$\Psi(x,t) = e^{-\frac{iE_n t}{\hbar}}\psi_n(x)$	General solution to the Schrodinger equation

What to know about the wavefunction

- ψ_n for different eigenvalues are orthogonal (their integral equals zero)
- ψ is continuous, and the derivative usually also so
- ψ_0 is the ground state and has no nodes (place where the wavefunction vanishes)
- Even functions are symmetric about a vertical axis – varies by ψ_n

Operators

- … do not commute
- They are computed left to right, and can be used together
  [A,B] = AB - BA
- $[\hat{x}, \hat{p}\,] = i\hbar$ is the most important one
- Operators are involved in uncertainty, as in the Heisenberg uncertainty principle
  $\sigma_x \sigma_p \geq \frac{\hbar}{2}$, approximated by $\Delta x \Delta p \approx \hbar$ and $\Delta E \Delta t \approx \hbar$
- Also, ${\sigma_A}^2 = \langle A^2 \rangle - \langle A \rangle^2$

Quantum Harmonic Oscillator 1D

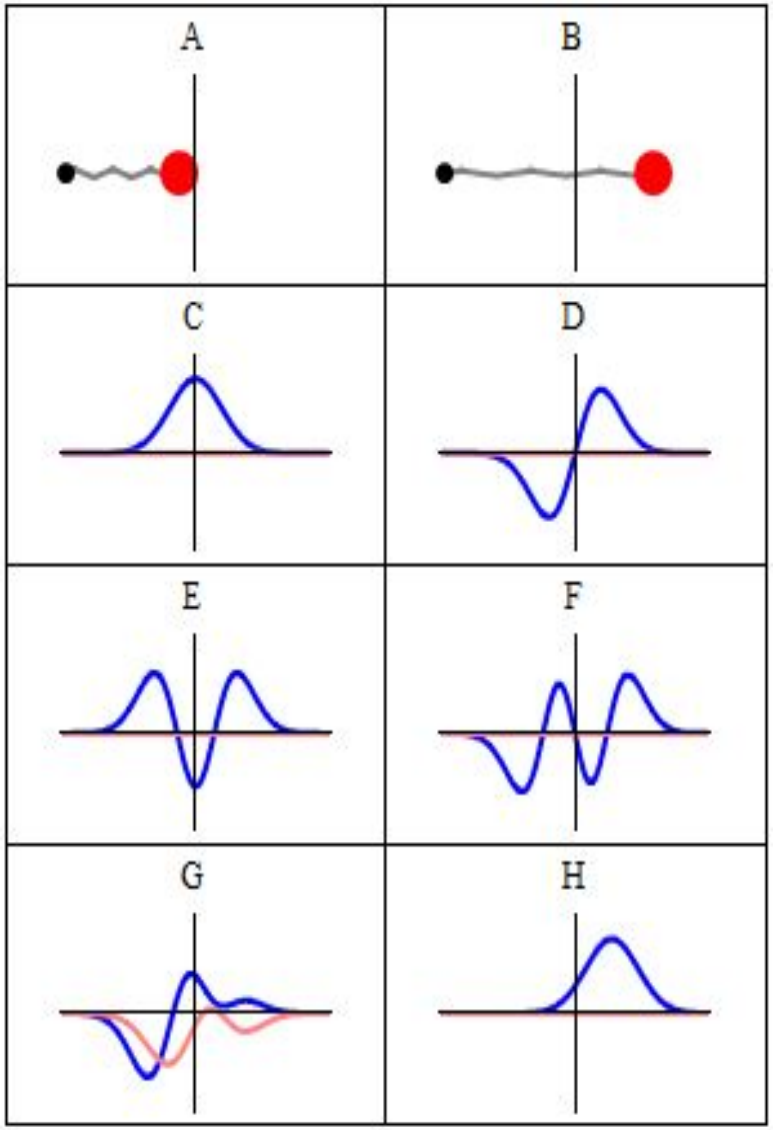
$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \qquad H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)$$

$$[a, a^\dagger] = 1 \qquad H|0\rangle = \frac{\hbar\omega}{2}|0\rangle$$

$$H|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle, \quad n = 0, 1, 2, \ldots$$

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle; \quad a|n\rangle = \sqrt{n}|n-1\rangle,$$

$$\langle T\rangle = \langle V\rangle = \frac{E_n}{2}.$$



Horizontal axis is position, and the vertical axis is the real part (blue) or imaginary part (red) of the wavefunction. C, D, E, F, but not G, H, are energy eigenstates. H is acoherent state—a quantum state that approximates the classical trajectory.

Quantum Harmonic Oscillator 3D

$$\psi_N(x,y,z) = \psi_{n_1}(x)\psi_{n_2}(y)\psi_{n_3}(z); \quad E_N = \left(N + \frac{3}{2}\right)\hbar\omega \text{ with } N = n_1 + n_2 + n_3.$$

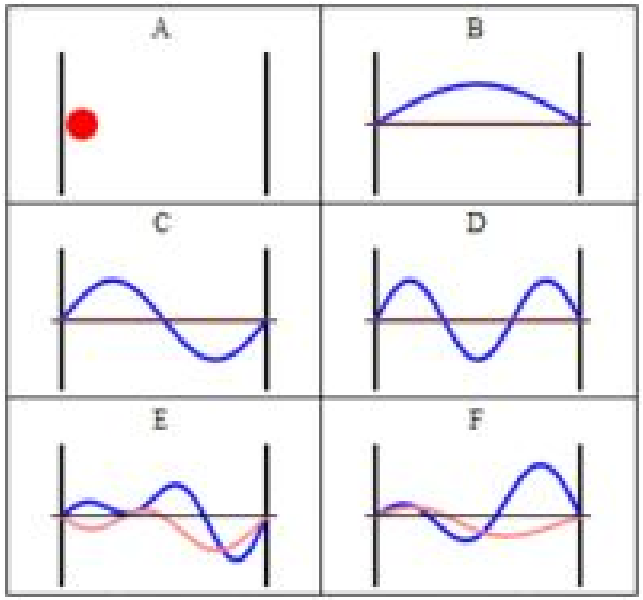
$$(n_1, n_2, n_3) = (1,0,0),\ (0,1,0),\ (0,0,1)$$

Infinite Square Well

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x), \quad V(x) = \begin{cases} 0, & 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases}$$

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

$$V(x,y,z) = \begin{cases} 0, & 0 \le x,y,z \le a \\ \infty, & \text{otherwise} \end{cases}$$



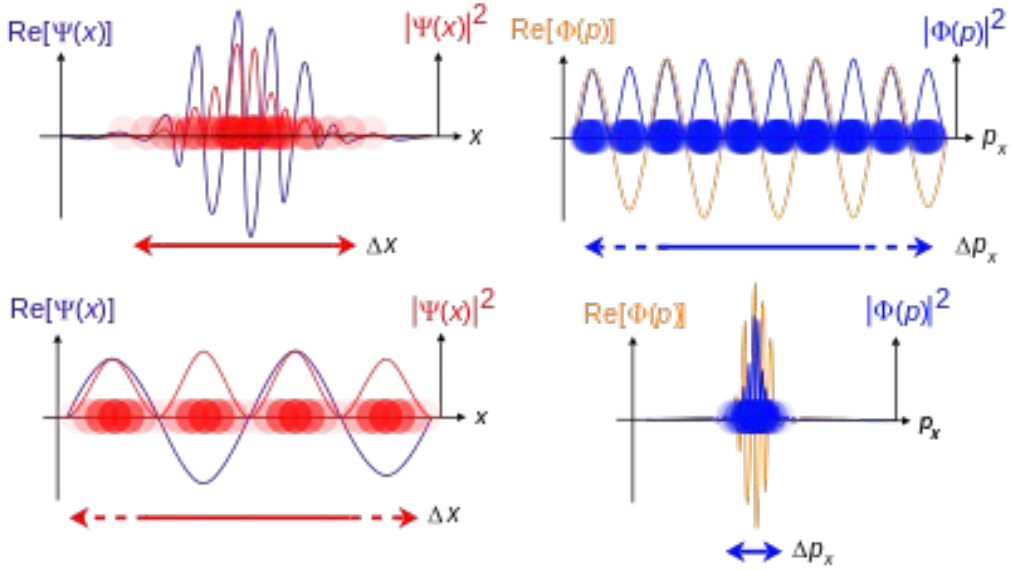
Horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B,C,D) are energy eigenstates, but (E,F) are not.

Free Particle

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}.$$

$$\psi(x) = e^{\pm ikx}, \quad E = \frac{\hbar^2 k^2}{2m}.$$

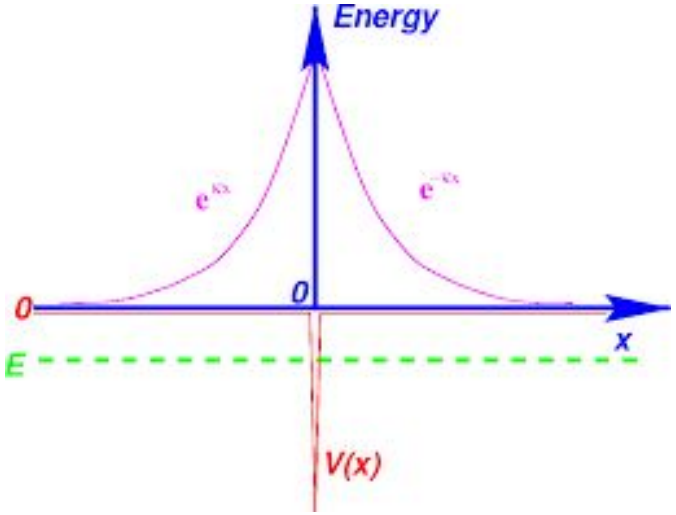
$$p = \hbar k,$$



Increasing amounts of wavepacket localization, meaning the particle becomes more localized.

Delta Function

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - A\delta(x),$$



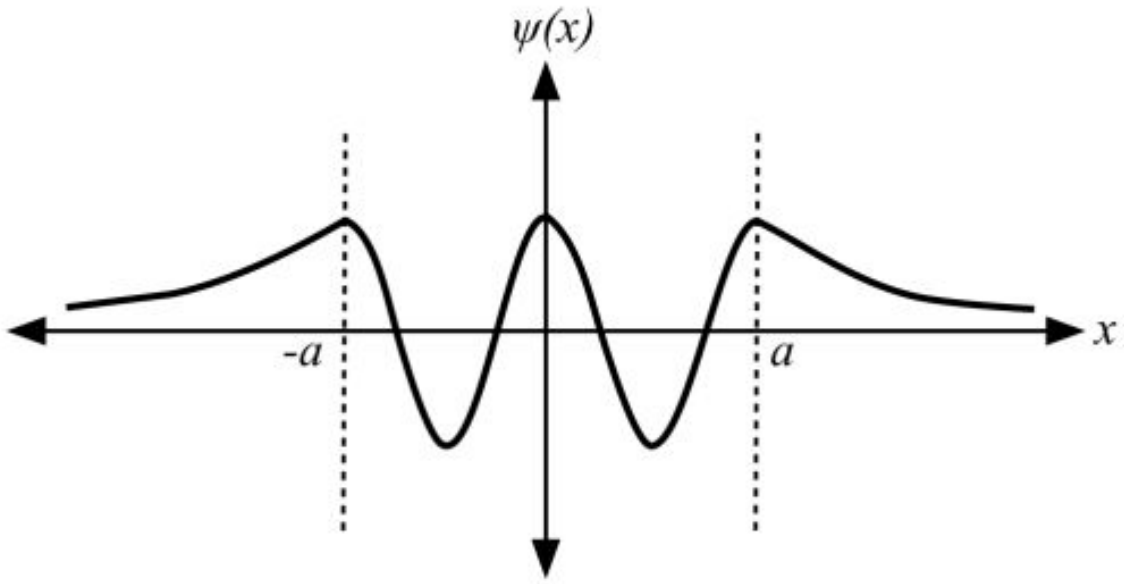
$$\int_{-\epsilon}^{\epsilon}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)\right)dx - A\int_{-\epsilon}^{\epsilon}\delta(x)\psi(x)\,dx = E\int_{-\epsilon}^{\epsilon}\psi(x)\,dx$$

$$\int_{-\epsilon}^{\epsilon}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)\right)dx - A\int_{-\epsilon}^{\epsilon}\delta(x)\psi(x)\,dx = -\frac{\hbar^2}{2m}\left(\frac{d\psi}{dx}\right)\Bigg|_{-\epsilon}^{\epsilon} - A\psi(0),$$

$$\psi(x) = \frac{\sqrt{mA}}{\hbar}e^{-mA|x|/\hbar^2}, \quad E = -\frac{mA^2}{2\hbar^2}.$$

Finite Square Well

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x), \quad V(x) = \begin{cases} -V_0, & -a \le x \le a \\ 0, & \text{otherwise} \end{cases}$$



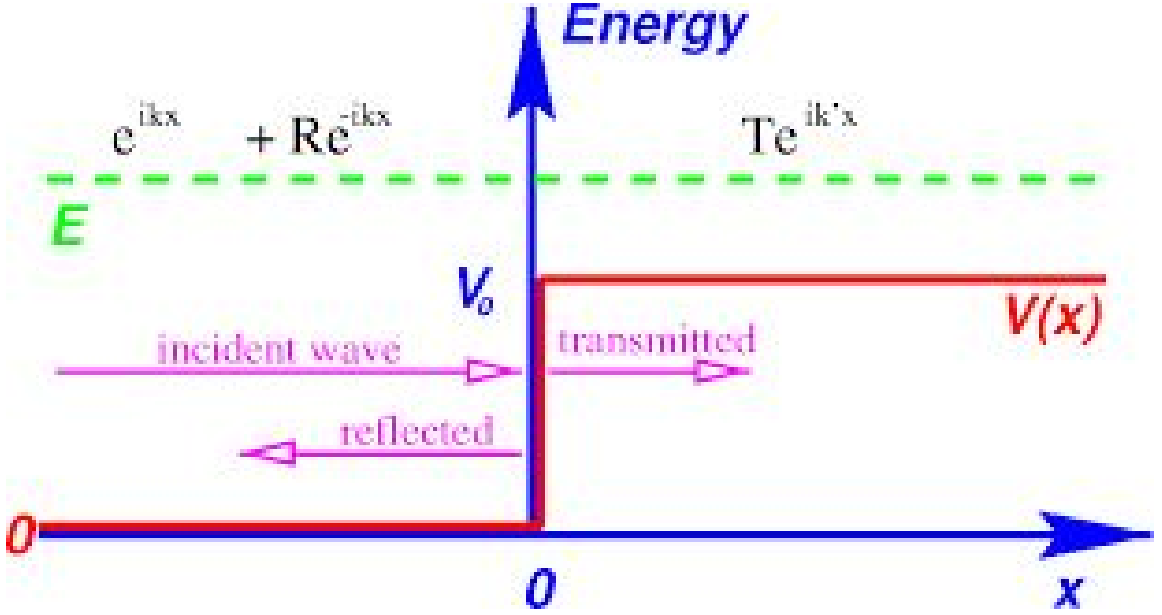
Wave function inside the well turning to decaying exponentials outside the well.

Scattering States: Reflection/Transmission

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x \le -a \\ \text{something}, & -a \le x \le a \\ Ce^{ikx}, & x \ge a \end{cases}$$

$$R = \frac{|B|^2}{|A|^2}, \quad T = \frac{|C|^2}{|A|^2}.$$

$$V(x) = \begin{cases} 0, & x \le 0 \\ V_0, & x \ge 0 \end{cases}$$



Three Dimensions

- Momentum Operator:

$$\hat{p} = -i\hbar\nabla$$

$$\nabla = \frac{\partial f}{\partial x}\hat{x} + \frac{\partial f}{\partial y}\hat{y} + \frac{\partial f}{\partial z}\hat{z}$$

Hamiltonian in 3D

$$H = \frac{-\hbar^2}{2m}\nabla^2 + V(r)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Different Coordinates Commute with Each Other

$$[\hat{x}, \widehat{p_x}] = [\hat{y}, \widehat{p_y}] = [\hat{z}, \widehat{p_z}] = i\hbar$$

$$[\hat{x}, \hat{y}] = [\hat{x}, \widehat{p_y}] = [\hat{x}, \widehat{p_z}] = 0$$

Spherical Wave Function

- Spherical Wave function: Product of angular and radial part

$$\psi(r) = R(r)\mathrm{Y}(\theta, \phi)$$

- Separate into radial and angular part and normalize each piece separately

$$\int_0^{2\pi} \int_0^{\pi} |\mathrm{Y}(\theta, \phi)|^2 \sin\theta \, d\theta \, d\phi = 1$$

$$\int_0^{\infty} |R(r)|^2 r^2 dr = 1$$

Angular Momentum

$$\hat{L} = \hat{r} \times \hat{p}$$

$$\widehat{L_x} = \hat{y}\widehat{p_z} - \hat{z}\widehat{p_y}$$

$$\widehat{L_y} = \hat{z}\widehat{p_x} - \hat{x}\widehat{p_z}$$

$$\widehat{L_z} = \hat{x}\widehat{p_y} - \hat{y}\widehat{p_x}$$

Something to Remember For GRE

$$[\widehat{L_x}, \widehat{L_y}] = i\hbar\,\widehat{L_z}$$

$$\widehat{L^2} = \widehat{L_x} + \widehat{L_y} + \widehat{L_z}$$

Spherical Coordinates

$$\widehat{L^2} = -\hbar^2 \nabla^2_{\theta,\phi}$$

$$\widehat{L_z} = i\hbar^2 \frac{\partial}{\partial \phi}$$

Eigenfunction and Eigenvalues

$$Y_l^m(\theta, \phi)$$

$$\widehat{L_z}\, Y_l^m = m\hbar\, Y_l^m$$

$$\widehat{L^2} Y_l^m = l(l+1)\hbar^2 Y_l^m$$

$$(m, l) \in \mathbb{Z}, l \geq 0$$

$$m = l, l-1, l-2, \ldots\ldots, -l$$

Some Facts

- Orthonormal:

$$\int_0^{2\pi}\int_0^{\pi} Y_l^m * Y_l^{m'} \sin\theta \, d\theta \, d\phi = \delta_{mm'}$$

$$\delta_{mm'} = \begin{cases} 0 \; if \; m \neq m' \\ 1 \; if \; m = m' \end{cases}$$

- The ϕ dependence is always in the form $e^{im\phi}$

- Dependence of θ is complicated and will be provided

Hydrogen Atom

- Hamiltonian:

$$H = \frac{-\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

- Bohr Radius

$$a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

Energy States

- Ground state energy (Hydrogen):

$$-E_1 = \frac{h^2}{2\,\mu\,a^2} = 13.6\ \text{eV}$$

- n state energy:

$$-E_n = \frac{\hbar^2}{2\,\mu\,a^2} * \frac{1}{n^2} \quad n = 1,2,3, \ldots.$$

Rydberg's Formula

$$f \propto \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|$$

Useful for GRE

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx {}^{1}/_{137}$$

Spin

Spin is a characteristic of a particle, and doesn't change!

Spin operators obey same commutation relations as angular momentum operators.

Spin can either be an integer or half-integer.

For GRE, only really need to know spin-½

Adding spins is not trivial:

For system of two particles (spin s and spin s')

$$s_{tot} = s + s', s + s' - 1, s + s' - 2, \ldots, |s - s'|$$

Spin-1/2

$$S_x = \frac{\hbar}{2}\sigma_x, \quad S_y = \frac{\hbar}{2}\sigma_y, \quad S_z = \frac{\hbar}{2}\sigma_z$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$|\Uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |\Downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} a \\ b \end{pmatrix} = a|\Uparrow\rangle + \mathrm{b}|\Downarrow\rangle$$

$$|\Uparrow\rangle_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, |\Downarrow\rangle_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$|\Uparrow\rangle_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}, |\Downarrow\rangle_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

Spin and the wavefunction

- Can think of total wavefunction as a product of a spatial wavefunction and a spin wavefunction
- Spin operators always commute with spatial operators
- If particle has spin-0, it only has a spatial wavefuntion

Note: the Hamiltonian can act on both the spin and spatial wavefunctions!

Bosons and fermions

Bosons	Fermions
Integer spin	Half-integer spin
Symmetric wavefunctions	Antisymmetric wavefunctions
Photons, alpha particles, deuterons	Electrons, muons, protons, neutrons

Pauli exclusion principle:

- no 2 identical fermions can occupy the same quantum state

For identical particles…

- symmetric wavefunctions: $\Phi(x_1, x_2) = \Phi(x_2, x_1)$
- antisymmetric wavefunctions: $\Phi(x_1, x_2) = -\Phi(x_2, x_1)$

Approximation Methods in QM

Variation principle

- Approx. ground state E of system when Hamiltonian known
- For a normalized wavefunction: $\langle\psi|\hat{H}|\psi\rangle \geq E_{gs}$
- Use trial wavefunction with adjustable parameter, calculate and minimize with respect to parameter

Adiabatic theorem

- For particle in nth eigenstate of H, if H is slowly changed to H', then particle will end up in the corresponding eigenstate

Note: will not have to apply variation principle on GRE!!

Time-independent perturbation theory

$$H = H_0 + \lambda H'$$

- $\lambda << 1$, know energies and eigenfunctions of H0, so can compute corrections
- First-order: $$E_n = E_n^0 + \lambda \langle \psi_n^0 | H' | \psi_n^0 \rangle$$
- Second-order: $$E_n = E_n^0 + \lambda^2 \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$$
  - If there is a degeneracy, denominator $= 0$
  - Diagonalize the perturbation in the subspace of degenerate states!

$$H'_{degen} = \begin{pmatrix} H'_{aa} & H'_{ab} \\ H'_{ba} & H'_{bb} \end{pmatrix} \equiv \begin{pmatrix} \langle \psi_a | H' | \psi_a \rangle & \langle \psi_a | H' | \psi_b \rangle \\ \langle \psi_b | H' | \psi_a \rangle & \langle \psi_b | H' | \psi_b \rangle \end{pmatrix}$$

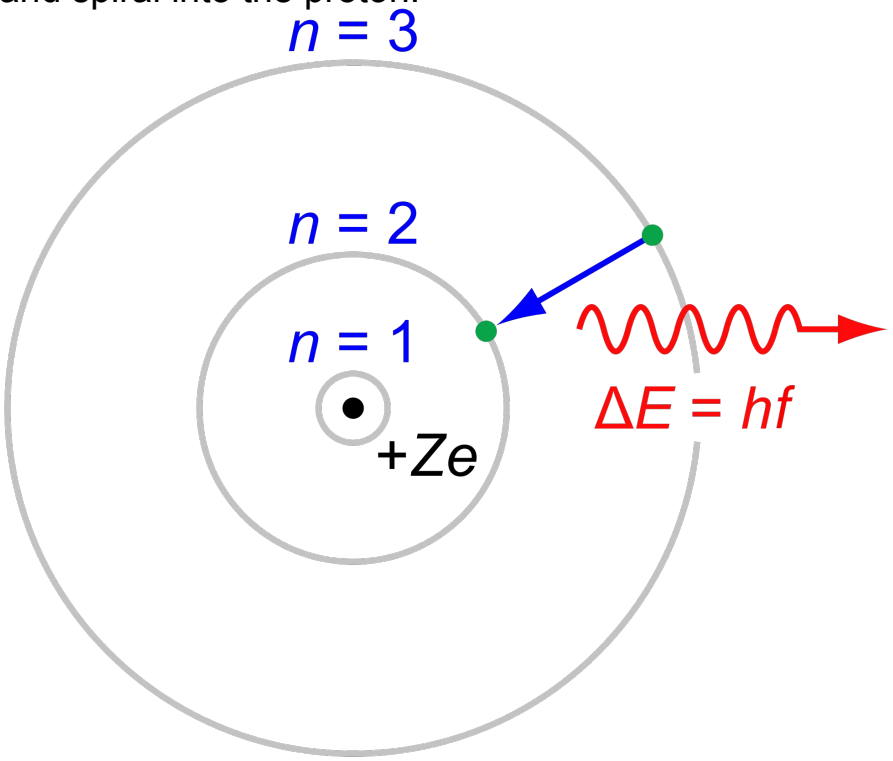
Atomic Review

Bohr Model

- Electrons move in *classical* circular orbits, called energy shells or energy levels.
- Angular Momentum - L=n*ħ where n=1,2,3…
- Electrons do not radiate as they move around the nucleus.
  - Classically the electron would radiate and spiral into the proton.

Angular Momentum

- L=mvr



Number	Symbol	Possible Values
Principal Quantum Number	n	$1, 2, 3, 4, \ldots$
Angular Momentum Quantum Number	ℓ	$0, 1, 2, 3, \ldots, (n-1)$
Magnetic Quantum Number	m_l	$-\ell, \ldots, -1, 0, 1, \ldots, \ell$
Spin Quantum Number	m_s	$+1/2, -1/2$

Perturbations to the Hydrogen Atom

Fine Structure

- Replacing the electron KE term in the Hamiltonian with the correct relativistic form.
- Spin-Orbit coupling between electron's orbital angular momentum and its spin.

Lamb Shift

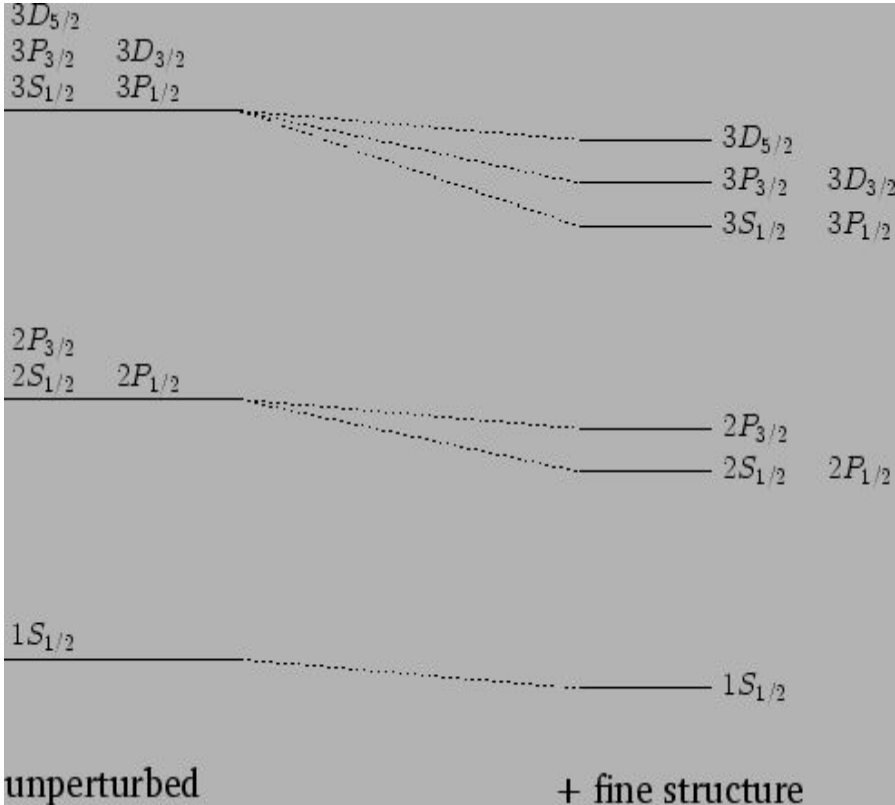
- Splits the 2s and 2 level with j=½.

Spin-Spin Coupling

- Ground state of hydrogen splits.
- Depends on spins of e and p.

Useful Calculation Tip

- $J^2=(\mathbf{L}+\mathbf{S})^2$
- $=L^2+2\mathbf{L}\cdot\mathbf{S}+S^2$
- $\mathbf{L}\cdot\mathbf{S}=\frac{1}{2}(J^2-L^2-S^2)$



Shell Model and Electronic Notation

Orbitals

- s→∠ = 0
- p→∠ = 1
- d→∠ = 2
- f →∠ = 3

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Principal Quantum Number	n	$1, 2, 3, 4, \ldots$
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Magnetic Quantum Number	m_l	$-\ell, \ldots, -1, 0, 1, \ldots, \ell$
Spin Quantum Number	m_s	$+1/2, -1/2$

$L=n\hbar \quad L^2=l(l+1)\hbar^2 \quad |L|=\hbar\sqrt{2}$

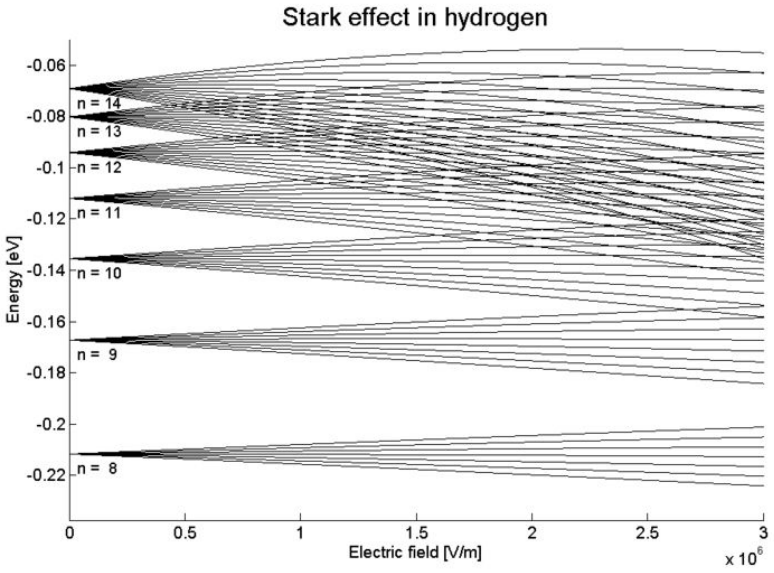
$$1s\,{}^{2}_{2}\,2s\,{}^{2}_{4}\,2p\,{}^{6}_{10}\,3s\,{}^{2}_{12}\,3p\,{}^{6}_{18}\,4s\,{}^{2}_{20}\,3d\,{}^{10}_{30}\,4p\,{}^{6}_{36}\,5s\,{}^{2}_{38}\,4d\,{}^{10}_{48}\,5p\,{}^{6}_{54}\,6s\,{}^{2}_{56}\,4f\,{}^{14}_{70}\,5d\,{}^{10}_{80}\,6p\,{}^{6}_{86}\,7s\,{}^{2}_{88}\,5f\,{}^{14}_{102}\,6d\,{}^{10}_{112}\,7p\,{}^{6}_{118}$$

Shells fill in order, preferring smaller values of l until Argon.

Noble gases are chemically inert because they have totally filled electron shells.

- Alkali metals have one “extra” electron
- Halogens have one fewer electron

Stark Effect



Splitting of degenerate energy levels caused by E-field.

Change in Hamiltonian in a uniform electron field is given by,

- $\Delta H = e\mathbf{E} \cdot \mathbf{r}$

There is no change in the ground state energy

First states to show a first-order shift are n=2 states.

- States with m=±1 are unaffected, but 2s and 2p states with m=0 are split.

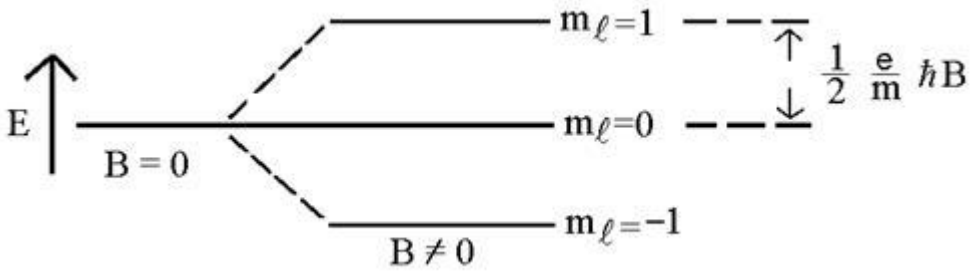
Energy splitting must be given of the form,

- $\Delta E = k e |\mathbf{E}| d$, where d is some length (usually $d = a_0$), and k is an undetermined constant.

Zeeman Effect

- Splitting of degenerate energy levels caused by B-field.

- Change in Hamiltonian in a magnetic field is given by,
  - $\Delta H=(e/2m)*(\mathbf{L}+2\mathbf{S})\cdot\mathbf{B}$
  - e/2m is the electron's classical *gyromagnetic ratio.*
  - 2 in front of spin operator is because the quantum gyromagnetic ratio is twice the classical value.



Selection Rules

- No transitions occur unless,
  - $\Delta m = \pm 1$ or 0
    - Conservation of the z-component of angular momentum
    - Photon Spin = 1 $\rightarrow \ell$ = -ħ, 0, ħ
  - $\Delta \ell = \pm 1$

- Decay Pattern Example:
  - 3s → 2p → 1s

Blackbody Radiation

$$I(\omega) \propto \frac{h\omega^2}{c^2} \frac{1}{e^{\frac{\hbar\omega}{k_b T}} - 1}$$

$$\frac{dP}{dA} \propto T^4$$

$$\lambda_{max} T = 2.9x10^{-3}\ K \cdot m$$