<table>
<thead>
<tr>
<th>Chapter</th>
<th>Reading</th>
<th>Questions/Problems, including Special labelled S1, S2,...</th>
</tr>
</thead>
<tbody>
<tr>
<td>1—Origins</td>
<td>All sections</td>
<td>Basics of classical physics &amp; challenges to it. Problem: Show that the exponential solutions to the e.m. wave equations in fact are valid solutions to it (see lecture slide)</td>
</tr>
<tr>
<td>3—Expts. Leading to quantum theory</td>
<td>Sections 3.1,3.3, 3.4, 3.5,3.6, 3.7,3.9 plus Section 14.8 on Accelerators, Synchrotrons, Linear Accelerators, pp. 533-536 (pp. 546-548), not including Fixed Target Accelerators</td>
<td>Probs. in Chap. 3: 2,9,14,17,19,23, plus special part of 23: If the emissivity of tungsten is 0.32 at this temperature, and the wire has a diameter of 0.01 cm, what length of wire would be necessary for a 60W bulb? 32,34,38,43 (Use 20,000 volts), 54 Probs. in Ch. 14: 31 and 34</td>
</tr>
<tr>
<td>2—Special relativity</td>
<td>Review entire chapter, but emphasis on 2.3, 2.5, 2.7, 2.8, 2.10-2.14, plus review from 12.6 on radioactive decay</td>
<td>Probs. In Chap. 2: 19, 25, 37, 51, 54,55, 54,55,57,68,76, plus problem 12.26 (12.28)</td>
</tr>
<tr>
<td>12—Radioactive decay</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15—General relativity</td>
<td>15.1-15.4, 15.5—optional (relates to newspaper article in S.F. Chronicle of April 5, 2004- see lecture slides)</td>
<td>Probs. in Chap. 15: 2,4,9,11 (13),17 (21),24 (28)—plus for this problem, what is the frequency change due to velocity? Use equations in lecture for GPS.</td>
</tr>
<tr>
<td>4—Structure of the atom</td>
<td>4.1-4.6</td>
<td>Probs. in Chap. 4: 11,23-Use 410 nm,29,32,38</td>
</tr>
<tr>
<td>5—Wave properties of matter</td>
<td>All sections, plus supplementary reading on Fourier integrals</td>
<td>Probs. in Chap. 5: 1-Use 15°, 3, 10, 11, 12, 17, 19, 22, 25, 27, 28, 33, 40, 43, 45, 48 54(52), plus Special Problems: S1-With reference to the website: <a href="http://www.falstad.com/fourier/index.html">http://www.falstad.com/fourier/index.html</a>, calculate the first two non-zero Fourier coefficients in the cosine+sine series representing a square wave, and show that they agree with the numbers given at this site. Why are there no cosine terms? S2-With reference to the supplementary reading on Fourier integrals, show that the final formula for g(ω) on p. 3 and plotted in 4.20 is correct.</td>
</tr>
<tr>
<td>6—Quantum theory</td>
<td>All sections</td>
<td>Probs. in Chap. 6: S1-Show that the wave function for a free particle traveling to the right is an eigenfunction of the momentum operator and the kinetic energy operator ,2,5,7,8,9,11,15,20,23,26,28,32 (34),37(39), 40(42),41(43),47(51),54(62)</td>
</tr>
<tr>
<td>7—The hydrogenic atom</td>
<td>All, plus supplementary reading on electronic transitions and selection rules (see link at website).</td>
<td>Questions: 1,2 Probs. in Chap. 7: 1,3,5,8,11,13,15,16,19 (Do for a 4p state),20,29,32,35,38,46, plus S1: Show, using the full hydrogenic atom wave functions given in a lecture slide that, if you take the combinations 3d_x+3d_y and 3d_y-3d_x, you get two of the real 3d orbitals, also shown in a lecture slide, and identify which ones.</td>
</tr>
</tbody>
</table>
**Question: 5**

Probs. in Chap. 8: 1,2,4 (Do argon and krypton), 5,7 (Do potassium, vanadium, selenium, zirconium, samarium, uranium), 11 (Do (a) $4s^24p^2$, (b) $4p^64d^{10}5s^1$ and (c) $5s^24p^64f^{11}$), 12, 23 (Remember the dipole selection rules!), 24 (Do for 1.7 Tesla).

S1: Let $\hat{P}_{12}$ be the permutation operator for the labelling of two identical particles that occupy the same region in space, which is defined from $\hat{P}_{12}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$. Now let $\hat{P}_{12}$ act on the following to determine which would be suitable choices for a wave function for two overlapping fermions (e.g. electrons, protons, or neutrons) or for two overlapping bosons (e.g., photons or pions) or for neither. Good wave functions must either be antisymmetric for fermions (-1 eigenvalue of $\hat{P}_{12}$) or symmetric for bosons (+1 eigenvalue of $\hat{P}_{12}$). Here, $\psi_{n/m_{\psi},+}(\vec{r}_1)$ represents particle 1 in spatial wavefunction $\psi_{n/m_{\psi},+}$ and with spin up ($m_s = +1/2$), $\psi_{n/m_{\psi},-}(\vec{r}_2)$ represents particle 2 in spatial wavefunction $\psi_{n/m_{\psi},-}$ and with spin down ($m_s = -1/2$), etc., etc. (See handout for further discussion.)

(a) $\psi(\vec{r}_1, \vec{r}_2) = \psi_{100,+}(\vec{r}_1)\psi_{100,-}(\vec{r}_2) - \psi_{100,+}(\vec{r}_2)\psi_{100,-}(\vec{r}_1)$

(b) $\psi(\vec{r}_1, \vec{r}_2) = \psi_{100,+}(\vec{r}_1)\psi_{100,+}(\vec{r}_2)$

(c) $\psi(\vec{r}_1, \vec{r}_2) = \psi_{210,+}(\vec{r}_1)\psi_{21-1,-}(\vec{r}_2) - \psi_{21-1,-}(\vec{r}_1)\psi_{210,+}(\vec{r}_2)$

(d) $\psi(\vec{r}_1, \vec{r}_2) = \psi_{210,+}(\vec{r}_1)\psi_{21-1,-}(\vec{r}_2)$.

S2: Show that the simple two-electron wave function for the ground state of He introduced in lecture is in fact normalized.
No. students

<table>
<thead>
<tr>
<th>Grade</th>
<th>Midterm</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>83</td>
</tr>
<tr>
<td>Ave.</td>
<td>54</td>
</tr>
<tr>
<td>Low</td>
<td>25</td>
</tr>
<tr>
<td>S.D.</td>
<td>13</td>
</tr>
</tbody>
</table>
Instructions for 2015 SHE-and-friends voluntary
tour of the Lawrence Berkeley National Laboratory
Saturday, 7 March, 2015

Anyone wishing to participate must send the name and citizenship/immigration status of themselves and any guests to Chuck by the Thursday just before the tour. You must also sign a liability waiver form that is attached to this form and send it to me: fadley@physics.ucdavis.edu. Please also bring a valid photo ID with you to the Lab.

The tour will last from 10:00 am until about 4:30 pm, and will include a lecture and videos on the Laboratory overall, as well as tours of the Advanced Light Source and the National Center for Electron Microscopy.

If you would like to come, all you need to do is either arrange your own individual transportation or get into a carpool. People who have cars are usually willing to take extra people, and we will as the day approaches try to get people who need rides together with those that have extra space in cars. Others outside of the class may also be driving from Davis.

IF DRIVING ON YOUR OWN: Directions and maps are as follows (with supplementary maps galore at:
http://www.lbl.gov/Workplace/lab-site-map.html):

- Leave Davis no later than 8:30 am Saturday so as to be able to arrive at LBNL for sure by 10:00 am.
- Take I-80 West and get off at the University Avenue exit in Berkeley.
- Follow University east until it ends at the UCB campus and Oxford Street.
- Turn left on Oxford Street.
- Turn right at the first intersection (a stoplight) onto Hearst Avenue.
- Go uphill on Hearst past two lights at Euclid and Gayley Road; the road changes name to Cyclotron Road. Keep on winding uphill past LBNL sign on left.
- Stop at the guardhouse (the Blackberry Gate) and identify yourself as part of the UC Davis Physics Tour. You will need a valid picture ID to get through the gate.
- Take the red route on the map. Also, you will begin to see signs "UC Davis Physics" with directional arrows posted at each intersection. (The orange route is an alternate via Gayley Road.)
- Go on uphill on Chu Road to the right to a roundabout; go right at the roundabout onto Smoot Road
- Go on uphill and go to the left at the next intersection (with a tree in the middle of the intersection) so as to continue on Smoot Road
- Go right at the next intersection, still uphill, and still on Lawrence Road. (Watch this one, as some people have gone on uphill to the left and gotten lost for a little while.)
- Take the first left and park in the Bldg. 2 parking lot.
- Go into the building and make yourself comfortable in the Conference Room 2-100B, where the tour will begin.
- On rare occasions, the Blackberry Gate will be closed for construction projects, and if so, you should take the orange route along Gayley Road, then left on Stadium Rim Road to pass along above the UC Stadium, left at the top onto Centennial Drive to what is finally a right turn into the Strawberry Gate entrance.

IF USING PUBLIC TRANSPORT: There are a few options.

- There is a Davis/Berkeley Shuttle bus, $11.00 with schedules at http://fleet.ucdavis.edu/bus/schedule, but it only runs to/from Berkeley once on Saturday mornings. Thus, you would have to stay overnight in Berkeley and come back the next day. If you are interested in this, make reservations as soon as possible, as it tends for overbook. From the bus dropoff, you need either walk up Hearst Avenue to
Blackberry Gate, or take an LBNL Blueline bus to stop at Bldg. 54 at the Lab., with schedules at: http://www2.lbl.gov/Workplace/Facilities/Support/Busses/all_routes.html

- Alternatively, one can take the train from Davis to Berkeley, $24.00, with schedules at http://www.amtrak.com/servlet/ContentServer2?pagename=am/am2Station/Station_Page&code=DAV, but this leaves you off at the Amtrak Station at the bottom of University Avenue, and you need to take a 51B AC Transit Bus up to the UC Campus, with schedules at http://www.actransit.org/maps/schedule_results.php?rms_view_types=1&version_id=26&maps_category=2 &maps_line=51B&map_submit=Get+Schedule, and then an LBNL Blueline bus to stop at Bldg. 54 at the Lab, with schedules at: http://www2.lbl.gov/Workplace/Facilities/Support/Busses/all_routes.html.

- Or, you can change from Amtrak to BART in Richmond, and take the Richmond-Fremont or Richmond-Millbrae train to the Downtown Berkeley Station, and then take the LBNL Blueline bus from there to the Bldg. 54 stop at the Lab. This is probably the quickest solution.

But I hope that, as usual, most people can find a suitable ride to avoid all these complications.

Lunch will not be provided, but there is a large battery of vending machines from which sandwiches and other things can be purchased. It will be helpful to bring along change and/or dollar bills for this purpose, or to just tote your own lunch.

If you have problems or get lost, call Chuck at 510-334-8667. We hope to see you there!
Waiver of Liability, Assumption of Risk, and Indemnity Agreement

Waiver: In consideration of being permitted to participate in any way in
Tour of the Lawrence Berkeley National Laboratory on 7 March, 2015, through Physics 9HE
hereinafter called "The Activity", I, for myself, my heirs, personal representatives or assigns, do hereby release, waive, discharge, and covenant not to sue The Regents of the University of California, its officers, employees, and agents from liability from any and all claims including the negligence of The Regents of the University of California, its officers, employees and agents, resulting in personal injury, accidents or illnesses (including death), and property loss arising from, but not limited to, participation in The Activity.

Signature of Parent/Guardian of Minor Date Signature of Participant Date

Assumption of Risks: Participation in The Activity carries with it certain inherent risks that cannot be eliminated regardless of the care taken to avoid injuries. The specific risks vary from one activity to another, but the risks range from 1) minor injuries such as scratches, bruises, and sprains 2) major injuries such as eye injury or loss of sight, joint or back injuries, heart attacks, and concussions to 3) catastrophic injuries including paralysis and death.

I have read the previous paragraphs and I know, understand, and appreciate these and other risks that are inherent in The Activity. I hereby assert that my participation is voluntary and that I knowingly assume all such risks.

Indemnification and Hold Harmless: I also agree to INDEMNIFY AND HOLD The Regents of the University of California HARMLESS from any and all claims, actions, suits, procedures, costs, expenses, damages and liabilities, including attorney's fees brought as a result of my involvement in The Activity and to reimburse them for any such expenses incurred.

Severability: The undersigned further expressly agrees that the foregoing waiver and assumption of risks agreement is intended to be as broad and inclusive as is permitted by the law of the State of California and that if any portion thereof is held invalid, it is agreed that the balance shall, notwithstanding, continue in full legal force and effect.

Acknowledgment of Understanding: I have read this waiver of liability, assumption of risk, and indemnity agreement, fully understand its terms, and understand that I am giving up substantial rights, including my right to sue. I acknowledge that I am signing the agreement freely and voluntarily, and intend by my signature to be a complete and unconditional release of all liability to the greatest extent allowed by law.

Signature of Parent/Guardian of Minor Date Signature of Participant Date
Participant's Age (if minor) ____
The Hydrogenic Atom
Schroedinger Equation:
Polar Coordinates

Classically:

\[ \overrightarrow{L} = \overrightarrow{r} \times \overrightarrow{p} \]

is conserved
\[ \mu = \text{reduced mass} = \frac{m_e}{1 + \frac{m_e}{M_n}} \]

\[ V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \]

Quantum mechanically:

\[ \dot{\vec{L}} = \vec{p} \]

Center of mass

\[ r \sin\theta \cos\phi, r \sin\theta \sin\phi, r \cos\theta \]

Polar angle = \( \theta = \arccos(z/r) \)
Azimuthal angle = \( \phi = \arctan(y/x) \)

Converting to new coordinates

\[ \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = -\cos\theta r \times 2\pi = 4\pi \]
• **Use Separation of Variables:**

\[ \Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \]

- *Assumed Form*

• Substitute, rearrange \( \phi \):

\[ \frac{d^2 \Phi}{d\phi^2} + C \Phi = 0 \implies \Phi(\phi) = A e^{\pm i C \phi} \]

\[ \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i m_\phi \phi} \]  

\[ m_\phi = 0, \pm 1, \ldots \]  

[\Theta(\theta) = f(\theta) \text{ & } \Phi(\phi) = g(\phi) \text{ in text} ]
Solving for the $\phi$ part = $\Phi(\phi)$:

"Boundary" condition in $\phi$:

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

$$e^{im_\phi \phi} = e^{im_\phi (\phi + 2\pi)} = e^{im_\phi \phi} e^{im_\phi 2\pi}$$

If $m_\phi = 0, \pm 1, \pm 2, \ldots$
The Bohr Formula!

\[ \Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad [ \Theta(\theta) \equiv f(\theta) \text{ & } \Phi(\phi) \equiv g(\phi) \text{ in text} ] \]

- **Use Separation of Variables:**

\[ \Theta(\theta) = f(\theta) \quad \text{&} \quad \Phi(\phi) = g(\phi) \]

- **Assumed Form:**

- **Substitute, Rearrange \( \rightarrow \)**

\[ \Phi(\phi) = A e^{\pm i m_\phi \phi} \] \( \text{complex} \)

\[ C_\phi = m_\phi = 0, \pm 1, \ldots \]

\[ \Theta(\theta) \quad \text{for many-e- atoms} \]

\[ \frac{d^2 \Theta}{d \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{d \Theta}{d \theta} + \left[ \frac{\ell^2}{\sin^2 \theta} + \frac{\ell(\ell+1)}{\sin^2 \theta} \right] \Theta = 0 \]

\[ R = \left[ -\frac{\hbar^2}{2 \mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2 \ell + 1}{r} \frac{\partial}{\partial r} + \frac{\mu e^2}{4 \pi \varepsilon_0 r} \right) \right] R = E R \]

**A Radial Schrödinger Equation:**

\[ \hat{H}_{\text{radial}} R = E R \]

**The Bohr Formula!**

**The same for many-e- atoms**

**Changes for many-e- atoms**
Use separation of variables:
\[ \psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \]  
\[ \Theta(\theta) = f(\theta) \text{ and } \Phi(\phi) = g(\phi) \text{ in text} \]

Substitute, rearrange →
\[ \phi : \ \frac{d^2 \Phi}{d\phi^2} + C_\phi^2 \Phi = 0 \Rightarrow \Phi(\phi) = Ae^{\pm im_\phi \phi} \]
\[ C_\phi^2 = m_\phi^2 = 0, \pm 1, \pm 2, \ldots \]

\[ \Theta : \ \frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta \frac{d}{d\theta}) \Theta + \left[ \frac{C_\theta}{\sin^2 \theta} - \frac{m_\phi^2}{\sin^2 \theta} \right] \Theta = 0 \]
\[ l(l+1) \rightarrow Z_{\text{eff}}(r) \text{ in many e}^- \text{ atom} \]

\[ R : \left[ -\frac{1}{2\mu} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{l(l+1)}{2\mu r^2} - \frac{Ze^2}{4\pi \epsilon_0 r} \right] R = Er \]
A "radial Schrödinger eqn."

Solving for \( \Theta \) with 2 ⇒

\[ \Theta_{2m_\phi}(\theta) = \text{assoc. Legendre polynomials in } (\cos \theta) - \text{real} \]
\[ l = 0, 1, 2, 3, \ldots (n-1) \]
\[ m_\phi = -l, -l+1, \ldots 0 \ldots + l-1, l \]

Solving for \( R \) with 3 ⇒

\[ R_{n_\phi}(r) = \text{assoc. Laguerre functions also} \]
\[ = \text{polynomial in } r_\phi e^{-r_\phi/2} \text{ -real} \]

Changes for many-e\(^-\) atoms

The Bohr Formula!
The same for many-e\(^-\) atoms

Slide Set 5
12
In many-electron atoms:
For a given n, s feels nuclear charge
more than p, more than d, more than f

Lifts degeneracy on \( \ell \) in hydrogenic atom

\[ k_C \equiv \frac{1}{(4\pi\varepsilon_0)} \]
GROUND STATE OF HYDROGENIC ATOM:
\[ \psi_{100} = R_{10}(r) Y_0^0(\theta, \phi) = \pi^{-1/2} \left( \frac{2}{a_0} \right)^{3/2} e^{-\frac{2r}{a_0}} \]

Most probable \( r = \text{Bohr orbit radius} \)

\[ P_{1s} = (R_{10}(r))^2 r^2 \]

\[ |\psi_{100}|^2 = \frac{Z^3}{\pi a_0^3} e^{-2Zr/a_0} \]

\( E = E_{100} = \text{Bohr energy for } n = 1! \)
The atomic orbitals:

$$e^{-r/na_0} \rightarrow e^{-Zr/na_0}$$ for hydrogenic

$$Z \rightarrow Z_{\text{eff}}(r)$$ in many-e\(^{-}\) atoms

Table 6.1

<table>
<thead>
<tr>
<th>(n)</th>
<th>(\ell)</th>
<th>(m)</th>
<th>(\Phi(\phi))</th>
<th>(\Theta(\theta))</th>
<th>(\mathcal{R}_{\ell m}(r))</th>
<th>(\Psi_{n\ell m}(r,\theta,\phi))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>±0</td>
<td>$1/\sqrt{2\pi}$</td>
<td>$1/\sqrt{2}$</td>
<td>$2/\sqrt{2}a_0^2 e^{-r/a_0}$</td>
<td>$1/\sqrt{\pi}a_0^{-2} e^{-r/a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>±0</td>
<td>$1/\sqrt{2\pi}$</td>
<td>$1/\sqrt{2}$</td>
<td>$1/2\sqrt{2}a_0^{-2} (2 - r/a_0) e^{-r/2a_0}$</td>
<td>$1/4\sqrt{2}\pi a_0^{-2} (2 - r/a_0) e^{-r/2a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>±1</td>
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<td>$1/2 \cos \theta$</td>
<td>$1/2 \sqrt{6}a_0^{-2} e^{-r/2a_0}$</td>
<td>$1/\sqrt{4}\sqrt{2}\pi a_0^{-2} \sqrt{6}a_0^{-2} e^{-r/2a_0} \sin \theta e^{\pm i\theta}$</td>
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<tr>
<td>3</td>
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<td>$1/\sqrt{2}$</td>
<td>$1/8\sqrt{3}a_0^{-1} (27 - 18 r/a_0 + 2 r^2/a_0^2) e^{-r/3a_0}$</td>
<td>$1/8\sqrt{3}\pi a_0^{-2} (27 - 18 r/a_0 + 2 r^2/a_0^2) e^{-r/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>±1</td>
<td>$1/\sqrt{2\pi}$</td>
<td>$1/2 \sin \theta$</td>
<td>$1/8\sqrt{6}a_0^{-1} (6 - r/a_0) e^{-r/3a_0} \cos \theta$</td>
<td>$1/8\sqrt{6}\pi a_0^{-2} (6 - r/a_0) e^{-r/3a_0} \cos \theta e^{\pm i\theta}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>±1</td>
<td>$1/\sqrt{2\pi}$</td>
<td>$1/2 \sin \theta$</td>
<td>$1/8\sqrt{10}a_0^{-1} (3 \cos^2 \theta - 1) e^{-r/3a_0}$</td>
<td>$1/8\sqrt{10}\pi a_0^{-2} (3 \cos^2 \theta - 1) e^{-r/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>±1</td>
<td>$1/\sqrt{2\pi}$</td>
<td>$1/2 \sin \theta \cos \theta$</td>
<td>$1/8\sqrt{15}a_0^{-1} r^2 e^{-r/3a_0}$</td>
<td>$1/8\sqrt{15}\pi a_0^{-2} r^2 e^{-r/3a_0}$</td>
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<tr>
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<td>$1/2 \sin \theta \cos \theta$</td>
<td>$1/8\sqrt{30}a_0^{-1} r^2 e^{-r/3a_0}$</td>
<td>$1/8\sqrt{30}\pi a_0^{-2} r^2 e^{-r/3a_0}$</td>
</tr>
</tbody>
</table>

*The quantity \(a_0 = 4\pi \varepsilon_0 \hbar^2/m e^2 = 5.3 \times 10^{-11}\) m is equal to the radius of the innermost Bohr orbit.

But we can make them real for convenience.
And for a **hydrogenic** atom: atomic no. \( Z \), one electron

\[
\psi_{100} = \frac{1}{\sqrt{\pi}} \frac{(Z)^{3/2}}{a_0} e^{-\frac{Zr}{a_0}}
\]

\[
\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}}
\]

\[
\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} Z \frac{r}{a_0} e^{-\frac{Zr}{2a_0}} \cos \theta
\]

\[
\psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} Z \frac{r}{a_0} e^{-\frac{Zr}{2a_0}} \sin \theta \ e^{\pm i\phi}
\]

\[
\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 27 - 18 \frac{Zr}{a_0} + 2 \frac{Z^2r^2}{a_0^2} \right) e^{-\frac{Zr}{3a_0}}
\]

\[
\psi_{310} = \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 6 - \frac{Zr}{a_0} \right) \frac{Zr}{a_0} e^{-\frac{Zr}{3a_0}} \cos \theta
\]

\[
\psi_{31\pm 1} = \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 6 - \frac{Zr}{a_0} \right) \frac{Zr}{a_0} e^{-\frac{Zr}{3a_0}} \sin \theta \ e^{\pm i\phi}
\]

\[
\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left( \frac{Z}{a_0} \right)^{3/2} Z \frac{Z^2r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} (3 \cos^2 \theta - 1)
\]

\[
\psi_{32\pm 1} = \frac{1}{81\sqrt{6\pi}} \left( \frac{Z}{a_0} \right)^{3/2} Z \frac{Z^2r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} \sin \theta \cos \theta \ e^{\pm i\phi}
\]

\[
\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} Z \frac{Z^2r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} \sin^2 \theta \ e^{\pm 2i\phi}
\]

These are written in terms of the parameter

\[
a_0 \equiv \frac{\hbar^2}{\mu_e^2} = 0.529 \times 10^{-8} \text{ cm}
\]

\[
\mu = \text{reduced mass} = \frac{m_e}{1 + \frac{m_e}{M_{\text{nucleus}}}}
\]

\[
E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}, \ n = 1, 2, 3, ...
\]

\[
\langle r_{nl} \rangle = \frac{n^2 a_0}{Z} \left[ 1 + \frac{1}{2} \left( 1 - \frac{\ell (\ell + 1)}{n^2} \right) \right]
\]

\[
= \frac{n^2 a_0}{Z}
\]

1.5 for 1s, 1.5 for 2s, 1.25 for 2p, ... converging to 1.0 for very large \( n \) and \( \ell_{\text{max}} = n - 1 \)

\[
(\text{Correspondence Principle limit})
\]

\[
r_{\text{Bohr}} = \frac{n^2 a_0}{Z}
\]
MAKING THE ATOMIC ORBITALS REAL (E.G., FOR CHEMICAL BONDING):

\[ \Psi_{nlm_e}(r, \theta, \phi) = R_{nl}(r) \Theta(\theta) \Phi(\phi) \]

COMPLEX

REAL

REAL

COMPLEX

IF \( m_e \neq 0 \)

So just take combo. of \( \pm m_e \) as:

\[ \Psi_{nlm_e}(r, \theta, \phi) = \frac{1}{2} [ \Psi_{nlm_e} + \Psi_{nl-m_e} ] \propto R_{nl} \Theta_{m_e} \cos m_e \phi \]

\[ \frac{1}{2i} [ \Psi_{nlm_e} - \Psi_{nl-m_e} ] \propto R_{nl} \Theta_{m_e} \sin m_e \phi \]

REAL

EXAMPLE: 2p ORBITALS

\[ \Psi_{210} = \Psi_{2p_0} = \Psi_{2p_2} \propto r \cos \theta = z \ (\text{ALREADY REAL}) \]

\[ \Psi_{211} = \Psi_{2p_1} \propto r \sin \theta e^{i\phi} = r \sin \theta [ \cos \phi + i \sin \phi ] \]

\[ \Psi_{21-1} = \Psi_{2p_{-1}} \propto r \sin \theta e^{-i\phi} = r \sin \theta [ \cos \phi - i \sin \phi ] \]

\[ \frac{1}{2} [ \Psi_{2p_{+1}} + \Psi_{2p_{-1}} ] = \Psi_{2p_x} \propto r \sin \theta \cos \phi = x \]

\[ \frac{1}{2i} [ \Psi_{2p_{+1}} - \Psi_{2p_{-1}} ] = \Psi_{2p_y} \propto r \sin \theta \sin \phi = y \]
And the same thing for the d orbitals:

\[ \propto r^2(3\cos\theta^2 - 1) = 3z^2 - r^2 \]

See special problem for Chap. 7

+ nodes for \( \cos\theta = 1/\sqrt{3} \)
\( \theta = 54.7^\circ, 125.3^\circ \)
The atomic orbitals:

\[ Y_{\ell m}(\theta,\phi) = \text{"spherical harmonics"} \]

But we can make them real for convenience.

### Table 6.1: Normalized Wave Functions of the Hydrogen Atom for \( n = 1, 2, \text{ and } 3^* \)

<table>
<thead>
<tr>
<th>( \ell )</th>
<th>( m )</th>
<th>( \phi (\phi) )</th>
<th>( \Theta_{\ell m}(\theta) )</th>
<th>( R_{n\ell}(r) )</th>
<th>( Y_{n\ell m}(r,\theta,\phi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>( \frac{1}{\sqrt{2\pi}} )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( \frac{2}{a_0^3} e^{-r/a_0} )</td>
<td>( \frac{1}{\sqrt{\pi} a_0^2} e^{-r/a_0} )</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>( \frac{1}{\sqrt{2\pi}} )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( \frac{1}{2\sqrt{2} a_0^3} (2 - \frac{r}{a_0}) e^{-r/2a_0} )</td>
<td>( \frac{1}{4\sqrt{2} a_0^2} (2 - \frac{r}{a_0}) e^{-r/2a_0} )</td>
</tr>
<tr>
<td>2</td>
<td>\pm 1</td>
<td>( \frac{1}{\sqrt{2\pi}} )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( \frac{1}{2\sqrt{6} a_0^3} \frac{r e^{-r/2a_0}}{a_0} )</td>
<td>( \frac{1}{8\sqrt{2} a_0^2} \frac{r e^{-r/2a_0}}{a_0} )</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>( \frac{1}{\sqrt{2\pi}} )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( \frac{2}{81\sqrt{3} a_0^3} (27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}) e^{-r/3a_0} )</td>
<td>( \frac{\sqrt{2}}{81\sqrt{3} a_0^2} (27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}) e^{-r/3a_0} )</td>
</tr>
</tbody>
</table>

*The quantity \( a_0 = \frac{4\pi e^2 n^2}{me^2} = 5.3 \times 10^{-11} \text{ m} \) is equal to the radius of the innermost Bohr orbit.*

- **Radial node for** \( r = 2a_0 \)
- **Angular node for** \( \theta = 90^\circ \)
- **Radial node for** \( r = 6a_0 \)
- **Angular nodes for** \( \cos^2 \theta = \frac{1}{3} \)
  \( \theta = 54.7^\circ, 125.3^\circ \)

**Z \rightarrow Z_{\text{eff}, \ell}(r) \text{ in many-}e^\text{- atoms}\)**

---

**Slide Set 5 19**
The Radial Parts $R_{n\ell}(r)$:

Figure 6.8: The variation with distance from the nucleus of the radial part of the electron wave function in hydrogen for various quantum states. The quantity $a_0 = \frac{4\pi\hbar^2}{me^2} = 0.053$ nm is the radius of the first Bohr orbit.
$P_{nl}(r) = r^2 |R_{nl}(r)|^2$ vs. $r$

**Figure 6.9** The probability of finding the electron in a hydrogen atom at a distance between $r$ and $r + dr$ from the nucleus for the quantum states of Fig. 6.8.

**General:**

$n - 2$ zeroes (incl. origin)

$P_{nl}$'s grouped in $K, L, M, \ldots$ "shells"

$n = 1, 2, 3, \ldots$
The Radial Probability Density

\[ P_{n\ell}(r) = r^2 R_{n\ell}(r)^2 : \]
The hydrogenic atom—putting it all together in three dimensions:

Figure 6.12 Shapes of some hydrogen-atom orbitals. The 2s orbital has a spherical node, which is not visible; the 3s orbital has two such nodes. The 3p, orbital has a spherical node (indicated by the dashed line) and a nodal plane (the xy plane). The 3d, orbital has two nodal cones; the 3d, orbital has two nodal planes. Note that the view shown is not the same for the various orbitals.
Some of the atomic orbitals, including radial dependence: Contours of equal probability in $|\psi|^2$, and angular parts.

See also: http://www.orbitals.com/orb/index.html
Aside on use of spherical harmonics as a complete set, like sines, cosines in Fourier analysis:

Expanding the Earth’s gravitational field in (real) spherical harmonics

\[
V = \frac{GM}{r} \left( 1 + \sum_{n=2}^{n_{\text{max}}} \left( \frac{a}{r} \right)^n \sum_{m=0}^{n} P_{nm}(\sin \theta) \left[ \overline{C}_{nm} \cos m\phi + \overline{S}_{nm} \sin m\phi \right] \right)
\]

n = 2 to 360, no n = 1 if center of mass at origin
Yields 130317 separate terms! Finally:

1 gal = 1 cm/s\(^2\) \approx 1/981 of mean gravitational accel.
Accurate to features of about 55 km in size
Comparison of three QM potential-well problems in 1 dimension

(a) Radial part of H atom

\[ E_n \propto \left(\frac{1}{n^2}\right) \]

\[ U(r) = -\frac{kZe^2}{r} - \frac{Ze^2}{4\pi\varepsilon_0 r} \]

(b) Rigid box

\[ E_n \propto n^2 \]

(c) Harmonic Oscillator

\[ E_n \propto (n + \frac{1}{2}) \]

\[ U(x) = \frac{1}{2}Kx^2 \]

Zero-point energies \( \neq 0 \)
EIGENFUNCTION PROPERTIES OF THE ATOMIC WAVEFUNCTIONS

Operator

Eigenvector

Energy: Hydrogenic atom - \( \hat{H}_\psi_{n\ell m_r} = E_n \psi_{n\ell m_r} \), \( E_n \) from Bohr formula, \( V(r) = \frac{Ze^2}{4\pi\varepsilon_o r} \)

Many-electron atom - \( \hat{H}_\psi_{n\ell m_r} = E_{n\ell} \psi_{n\ell m_r} \), \( E_{n\ell} \) from solution of radial Schroedinger with

\[ V_{\text{eff}}(r) = \frac{Z_{\text{eff},n\ell}(r)e^2}{4\pi\varepsilon_o r} \]

Square of angular momentum:
\[ \hat{L}^2 \psi_{n\ell m_r} = (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \psi_{n\ell m_r} = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi_{n\ell m_r} \]

\[ = \hbar^2 \ell (\ell + 1) \psi_{n\ell m_r} \]

\[ \rightarrow \text{Always measure same value: } \Delta(\hat{L}^2) = 0 \]

Z component of angular momentum:
\[ \hat{L}_z \psi_{n\ell m_r} = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \psi_{n\ell m_r} = -i\hbar \frac{\partial}{\partial \phi} \psi_{n\ell m_r} = \hbar m_r \psi_{n\ell m_r} \]

\[ \rightarrow \text{Always measure same value: } \Delta(L_z) = 0 \]

E.g. - \( n = 3, \ell = 2 \rightarrow ”3d” \)

Slide Set 5
Quantization of space:
The (randomly) precessing vector model:

- \( L_x, L_y, L_z \) CANNOT ALL BE CONSTANT: VIOLATES UNCERTAINTY PRINCIPLE
- ONLY \( L^2 \) (or \( |L| \)) + \( L_z \) CONSTANT

\[
L_z = \hbar m, \quad m = \pm 2, \pm 1, 0, \quad -1, -2
\]

\[
L^2 = \hbar^2 l(l+1) = \hbar^2 2(3)
\]

\[
|L| = \hbar \sqrt{L}
\]
EIGENFUNCTION PROPERTIES OF THE ATOMIC WAVEFUNCTIONS

**Energy** : Hydrogenic atom – \( \hat{H} \psi_{n \ell m_r} = E_n \psi_{n \ell m_r} \), \( E_n \) from Bohr formula, \( V(r) = \frac{Z e^2}{4 \pi \varepsilon_o r} \)

Many-electron atom – \( \hat{H} \psi_{n \ell m_r} = E_{n\ell} \psi_{n \ell m_r} \), \( E_{n\ell} \) from solution of radial Schroedinger with

\[
V_{\text{eff}}(r) = \frac{Z_{\text{eff},n\ell}(r)e^2}{4 \pi \varepsilon_o} \frac{1}{r}
\]

**Square of angular momentum** : \( \hat{L}^2 \psi_{n \ell m_r} = \hbar^2 \ell (\ell + 1) \psi_{n \ell m_r} \)

→ Always measure same value : \( \Delta(\hat{L}^2) = 0 \)

**Z component of angular momentum** : \( \hat{L}_z \psi_{n \ell m_r} = \hbar m_\ell \psi_{n \ell m_r} \)

→ Always measure same value : \( \Delta(L_z) = 0 \)

E.g. — \( n = 3, \ell = 2 \rightarrow \text{“3d”} \)

and finally

**Parity** : \( \hat{\Pi} \psi_{n \ell m_r}(\vec{r}) = \psi_{n \ell m_r}(-\vec{r}) = (-1)^\ell \psi_{n \ell m_r}(\vec{r}) \)

**Definition**

\( r, \theta, \phi \rightarrow r, \pi - \theta, \phi + \pi \)
Some of the atomic orbitals, including radial dependence:

- Contours of equal probability in $|\psi|^2$, and angular parts

See also:
http://www.orbitals.com/orb/index.html
## Degeneracy in the hydrogenic atom

<table>
<thead>
<tr>
<th>States</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 1$: $1s_0$</td>
<td>1</td>
</tr>
<tr>
<td>$n = 2$: $2s_0$, $2p_{+1}, 2p_0, 2p_{-1}$ (or $2s_0$, $2p_x, 2p_y, 2p_z$)</td>
<td>4</td>
</tr>
<tr>
<td>$n = 3$: $3s_0$, $3p_x, 3p_y, 3p_z$, $3d_{3z^2-r^2}, 3d_{x^2-y^2}, 3d_{xy}, 3d_{yz}, 3d_{xz}$</td>
<td>9</td>
</tr>
<tr>
<td>$n = \text{general}$</td>
<td>$n^2$</td>
</tr>
</tbody>
</table>
TRANSITIONS BETWEEN LEVELS AND SELECTION RULES:

\[ m, \Psi_m (r, t) = \psi_m (r, \theta, \phi) e^{-iE_m t / \hbar} \]

\[ n, \Psi_n (r, t) = \psi_n (r, \theta, \phi) e^{-iE_n t / \hbar} \]

During transition:

\[ \Psi (\vec{r}, t) = a(t) \Psi_m + b(t) \Psi_n \]

Then

\[ = \int \Psi^* \times \Psi \, dV \]

\[ \text{Emission} \]

See additional reading at website
And play with this nice online calculation tool, for both square well and coulomb potentials:

http://phet.colorado.edu/en/simulation/covalent-bonds

Set the potential to 1D coulomb and the barrier width to as small as possible, and mix the time-dependent ground and first excited states equally. Watch the charge oscillate from left to right.
TRANSITIONS BETWEEN LEVELS AND SELECTION RULES:

\[ \Psi_m(t) = \psi_m(r, \theta, \phi) e^{-iE_m t/\hbar} \]

\[ \Psi_n(t) = \psi_n(r, \theta, \phi) e^{-iE_n t/\hbar} \]

\[ h\nu_{mn} = E_n - E_m \]

\[ \Psi_{\text{total}}(t) = a(t) \Psi_m + b(t) \Psi_n \]

\[ 1 \rightarrow 0 \quad 0 \rightarrow 1 \]

\[ \langle x \rangle = \int \psi_n^* \times \psi_m \, dV \neq 0 \]

\[ \text{INTENSITY } \propto \left| \int \psi_n^* \times \psi_m \, dV \right|^2 \]

\[ \Rightarrow \text{"SELECTION RULES" OF:} \]

\[ l_{\text{FINAL}} = l_{\text{INITIAL}} \pm 1 \quad \text{or} \quad \Delta l = \pm 1 \]

\[ m_{l,\text{FINAL}} = m_{l,\text{INITIAL}} \quad \text{or} \quad \Delta m_l = 0, \pm 1 \]

x = "dipole operator"

See additional reading at website
Energy-level diagram for hydrogen showing transitions allowed by the selection rule $\Delta l = \pm 1$. In this diagram the vertical axis represents excitation energy above the ground state.
Bremsstrahlung
Copper, Molybdenum...
10-20 keV
Producing x-rays: the good old-fashioned way
+ Ze
1s 2p 3p e-
Line Spectra + a continuum
50-100 keV
How are these measured?
How do the 2 aspects arise?

Allowed: ΔL = -1

Forbidden: ΔL =
2s 0 → 1s
3s 0 → 1s
3d -2 → 1s

Line Spectra + a continuum
Bremsstrahlung
SPIN ANGULAR MOMENTUM: A LAST PROPERTY OF THE ELECTRON
THE STERN-GERLACH EXPERIMENT

Net forces:

Two allowed orientations of magnetic moment $\vec{\kappa}$ - spin angular momentum.
THE ELECTRON'S FINAL PROPERTY:
CHARGE = 1.602 X 10^{-19} C
MASS = 9.109 X 10^{-31} kg

+ ... SPIN ANGULAR MOMENTUM:
Quantum no. \( s = \frac{1}{2} \)

\[
|\vec{S}| = \hbar \sqrt{s(s+1)} = \hbar \sqrt{\frac{3}{4}}
\]

\( S_z = \pm \hbar / 2 \)

SPIN MAGNETIC MOMENT:
\[
\vec{\mu}_s = -\frac{e}{m_e} \vec{s} = -2\mu_B \frac{\vec{s}}{\hbar}
\]

with \( \mu_B = \frac{e\hbar}{2m_e} \)

= the Bohr magneton

= 9.274 x 10^{-28} J / T
THE ELECTRON'S FINAL PROPERTY:

CHARGE = 1.602 X 10^{-19} \text{ C}

MASS = 9.109 X 10^{-31} \text{ kg}

\[ \begin{align*}
\ldots \quad \text{SPIN ANGULAR MOMENTUM:} \\
\text{Quantum no. } s &= \frac{1}{2} \\
|\vec{s}| &= \hbar \sqrt{s(s+1)} = \hbar \sqrt{3/4} \\
S_z &= \pm \frac{\hbar}{2} \\
\text{SPIN MAGNETIC MOMENT:} \\
\vec{\mu}_s &= -\frac{e}{m_e} \vec{s} = -2\mu_B \frac{\vec{s}}{\hbar} \\
\text{with } \mu_B &= \frac{e\hbar}{2m_e} \\
\text{= the Bohr magneton} \\
\text{= 9.274x10}^{-28} \text{ J/T}
\end{align*} \]
The atomic orbitals:

\[ \psi_{n\ell m_m}(r, \theta, \phi, \text{spin}) = \psi_{n\ell m_m}(r, \theta, \phi) \times [\alpha(\uparrow) \text{ or } \beta(\downarrow)] \]

\[ Y_{\ell m}(\theta, \phi) = \text{"spherical harmonics"} \]

But we can make them real for convenience

| n | \ell | \ell \pm \frac{1}{2} | \ell \pm 
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>\frac{1}{\sqrt{2\pi}}</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>\frac{1}{\sqrt{2\pi}}</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>\frac{1}{\sqrt{2\pi}}</td>
<td>\pm \frac{1}{2}</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>\frac{1}{\sqrt{2\pi}}</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>\frac{1}{\sqrt{2\pi}}</td>
<td>\pm \frac{1}{2}</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>\frac{1}{\sqrt{2\pi}}</td>
<td>\pm \frac{1}{2}</td>
</tr>
</tbody>
</table>

The quantity \( a_0 = 4\pi\varepsilon_0 r^2/m_e^2 = 5.3 \times 10^{-11} \text{ m} \) is equal to the radius of the innermost Bohr orbit.

\[ e^{-r/na_0} \rightarrow e^{-Zr/na_0} \text{ for hydrogenic } Z \rightarrow Z_{\text{eff}}(r) \text{ in many-e}^{-} \text{ atoms} \]
Degeneracy in the hydrogenic atom with spin

<table>
<thead>
<tr>
<th>States</th>
<th>Degeneracy without spin</th>
<th>Degeneracy with spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>• $n = 1$: $1s_0$</td>
<td>Not</td>
<td>2</td>
</tr>
<tr>
<td>• $n = 2$: $2s_0, 2p_{+1,2p_0,2p_{-1}}$, or $2s_0, 2p_x, 2p_y, 2p_z$</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>• $n = 3$: $3s_0, 3p_x, 3p_y, 3p_z$, or $3d_{3z^2-r^2,3d_{x^2-y^2}}, 3d_{xy}, 3d_{yz}, 3d_{xz}$</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>• $n = \text{general}$</td>
<td>$n^2$</td>
<td>$2n^2$</td>
</tr>
</tbody>
</table>
ORBITAL ANGULAR MOMENTUM $\rightarrow$ ORBITAL MAGNETIC MOMENT

CLASSICAL
\[ \mu = iA \]

CURRENT LOOP

(b)
CLASSICAL
\[ \mu = iA \]

CURRENT LOOP
\[ \vec{\mu}_L = -\frac{e}{2m_e} \vec{L} = -\mu_B \frac{\vec{L}}{\hbar} \]

with: \[ \mu_B \equiv \frac{e\hbar}{2m_e} \equiv \text{the Bohr magneton} \]
Quantization of Space and the Zeeman Effect

Classical interaction of magnetic moment and B field:

(Young and Freedman, Ch. 27, Purcell, pp. 413-421)

\[ E = \text{potential energy} \]
\[ = -\vec{\mu} \cdot \vec{B} = -\mu B \cos \phi \]

\[ \therefore \text{Lowest energy for} \]
\[ \vec{\mu} \text{ parallel to} \vec{B} \]
Quantization of space:
The (randomly) precessing vector model:

- \( L_x, L_y, L_z \) cannot all be constant: violates uncertainty principle
- Only \( L^2 \) (or \( |L| \)) + \( L_z \) constant

\[
L_z = \hbar m_2, \quad m_2 = +2, +1, 0, -1, -2
\]

\[
L^2 = \hbar^2 l(l+1)
\]

\[
|L| = \hbar \sqrt{6}
\]
Classical interaction of magnetic moment and B field:
(Young and Freedman, Ch. 27 Purcell, pp. 413-421)

\[ E = \text{potential energy} = -\vec{\mu} \cdot \vec{B} = -\mu B \cos \phi \]

\[ \therefore \text{Lowest energy for } \vec{\mu} \text{ parallel to } \vec{B} \]
A FINAL (RELATIVISTIC) ATOMIC INTERACTION: SPIN-ORBIT COUPLING

(a) An electron circles an atomic nucleus, as viewed from the frame of reference of the nucleus. (b) From the electron's frame of reference, the nucleus is circling it. The magnetic field the electron experiences as a result is directed upward from the plane of the paper. The interaction between the electron's spin magnetic moment and this magnetic field leads to the phenomenon of spin-orbit coupling.
A FINAL (RELATIVISTIC) ATOMIC INTERACTION: SPIN-ORBIT COUPLING

(a) An electron circles an atomic nucleus, as viewed from the frame of reference of the nucleus. (b) From the electron’s frame of reference, the nucleus is circling it. The magnetic field the electron experiences as a result is directed upward from the plane of the paper. The interaction between the electron’s spin magnetic moment and this magnetic field leads to the phenomenon of spin-orbit coupling.

\[ \hat{H} = \hat{H}_{\text{kin}} + \hat{V} + \hat{H}_{\text{spin-orbit}} \]
\[ \hat{H}_{\text{spin-orbit}} \psi = E \psi \]

**Nuclear Rest Frame**

**Electron Rest Frame**

\[ B_L = \frac{\mu_i}{2\gamma} \]

\[ E_{S-O} = -\hat{r} \cdot \hat{B}_L \]

\[ E_{S-O} \propto \hat{S} \cdot \hat{L} \]

Adds to \( \hat{H} \) in Schröd. Eqn.
Spin-orbit coupling and a new angular momentum $J$

\[ H_{S-O} \]

$E_{S-O}$ COUPLES $S$ AND $L$ TO NEW "CONSERVED" $J$: 

\[ j = \ell \pm \frac{1}{2} \]

**Figure 8.12** (a) A vector model for determining the total angular momentum $J = L + S$ of a single electron. (b) The allowed orientations of the total angular momentum $J$ for the states $j = \frac{3}{2}$ and $j = \frac{1}{2}$. Notice that there are now an even number of orientations possible, not the odd number familiar from the space quantization of $L$ alone.

Eigenfunctions:

\[ \hat{J}^2 \Psi_{n,\ell,s=1/2,j,m_j} = \hbar^2 j(j+1) \Psi_{n,\ell,s=1/2,j,m_j} \]

\[ \hat{J}_z \Psi_{n,\ell,s=1/2,j,m_j} = \hbar m_j \Psi_{n,\ell,s=1/2,j,m_j} \]
Spin-orbit coupling and a new angular momentum J

\[ H_{SO} \]

\[ E_{SO} \]

Couples S and L to new "Conserved" J:

\[ j = \ell + \frac{1}{2} \]
\[ j = \ell - \frac{1}{2} \]

**Figure 8.12** (a) A vector model for determining the total angular momentum \( J = L + S \) of a single electron. (b) The allowed orientations of the total angular momentum \( J \) for the states \( j = \frac{3}{2} \) and \( j = \frac{1}{2} \). Notice that there are now an even number of orientations possible, not the odd number familiar from the space quantization of \( L \) alone.

\[ |J| = \sqrt{j(j+1)} \]

with:
\[ j = \{ \ell - \frac{1}{2}, \ell + \frac{1}{2} \} \]

\[ J_z = \pm m_j \]

with:
\[ m_j = -j, -j+1, \ldots, j \]

\[ 2j+1 \text{ DEGENERACY} \]

**GOOD QUANTUM NOS. IF \( E_{SO} \) STARGED**
EIGENFUNCTION PROPERTIES OF THE ATOMIC WAVEFUNCTIONS

Energy: Hydrogenic atom $\hat{H}_n \psi_{n\ell m \sigma} = E_n \psi_{n\ell m \sigma}$, $E_n$ from Bohr formula, $V(r) = \frac{Ze^2}{4\pi\varepsilon_o} \frac{1}{r}$

Many-electron atom $\hat{H}_n \psi_{n\ell m \sigma} = E_n \psi_{n\ell m \sigma}$, $E_n$ from solution of radial Schroedinger with

$$V_{\text{eff}}(r) = \frac{Z_{\text{eff},n\ell}(r)e^2}{4\pi\varepsilon_o} \frac{1}{r}$$

Square of angular momentum: $\hat{L}^2 \psi_{n\ell m \sigma} = (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \psi_{n\ell m \sigma} = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi_{n\ell m \sigma}$

$$= \hbar^2 \ell (\ell + 1) \psi_{n\ell m \sigma}$$

$\rightarrow$ Always measure same value: $\Delta(\hat{L}^2) = 0$

Z component of angular momentum: $\hat{L}_z \psi_{n\ell m \sigma} = -i\hbar (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) \psi_{n\ell m \sigma} = -i\hbar \frac{\partial}{\partial \phi} \psi_{n\ell m \sigma} = \hbar m \psi_{n\ell m \sigma}$

$\rightarrow$ Always measure same value: $\Delta(L_z) = 0$

$\psi_{n\ell m,ms}(r,\theta,\phi,\text{spin}) = \psi_{n\ell m}(r,\theta,\phi)x[\alpha(\uparrow) \text{ or } \beta(\downarrow)]$

with spin-orbit goes to $\hat{J}^2 \psi_{n,\ell,s=1/2,j,m_j} =$

$\hbar^2 j(j+1) \psi_{n,\ell,s=1/2,j,m_j}$

$\hat{J}_z \psi_{n,\ell,s=1/2,j,m_j} =$

$\hbar m_j \psi_{n,\ell,s=1/2,j,m_j}$
SPIN-ORBIT SPLITTING IN HYDROGEN 2p (SMALL!):

Figure 8.11 The 2p level of hydrogen is split by the spin-orbit effect into a doublet separated by the spin-orbit energy $\Delta E = 5 \times 10^{-5}$ eV. The higher energy state is the one for which the spin angular momentum of the electron is "aligned" with its orbital angular momentum. The 1s level is unaffected, since no magnetic field arises for orbital motion with zero angular momentum.

But larger in inner shells of heavy atoms: e.g., Fe (Z=26) - 2p$^{3/2}$ and 2p$^{1/2}$, $\Delta E = 43.1$ eV
LINE SPECTRA OF DIFFERENT SOURCES:

- Atomic hydrogen
- Sodium
- Helium
- Neon
- Mercury
- Molecular hydrogen = H₂

The Sun: blackbody emission plus absorption

Sodium- D-line emiss.

Sodium- D-line absorp.

WHY LINES?

FIGURE 38–20  Line spectra for the elements indicated and spectrum of the sun, showing absorption lines. (Courtesy of Bausch and Lomb Incorporated.)
EXAMPLE 8.4  The Sodium Doublet

The famed sodium doublet arises from the spin–orbit splitting of the sodium $3p$ level, and consists of the closely spaced pair of spectral lines at wavelengths of 588.995 nm and 589.592 nm. Show on an energy level diagram the electronic transitions giving rise to these lines, labeling the participating atomic states with their proper spectroscopic designations. From the doublet spacing, deduce the magnitude of the spin–orbit energy.

**Solution**  The outer electron in sodium is the first electron to occupy the $n = 3$ shell, and it would go into the lowest energy subshell, the $3s$ or $3S_{1/2}$ level. The next highest levels belong to the $3p$ subshell. The $2(2\ell + 1) = 6$ states of this subshell are grouped into the $3P_{1/2}$ level with two states, and the $3P_{3/2}$ level with four states. The spin–orbit effect splits these levels by the spin–orbit energy. The outer electron, once it is excited to either of these levels by some means (such as an electric discharge in the sodium vapor lamp), returns to the $3S_{1/2}$ level with the emission of a photon. The two possible transitions $3P_{3/2} \rightarrow 3S_{1/2}$ and $3P_{1/2} \rightarrow 3S_{1/2}$ are shown in Figure 8.13. The emitted photons have nearly the same energy, but differ by the small amount $\Delta E$ representing the spin–orbit splitting of the initial levels. Since $E = \hbar c / \lambda$ for photons, $\Delta E$ is found as

$$\Delta E = \frac{\hbar c}{\lambda_1} - \frac{\hbar c}{\lambda_2} = \frac{\hbar (\lambda_2 - \lambda_1)}{\lambda_1 \lambda_2}$$

For the sodium doublet, the observed wavelength difference is

$$\lambda_2 - \lambda_1 = 589.592 \text{ nm} - 588.995 \text{ nm} = 0.597 \text{ nm}$$

Using this with $\hbar c = 1240 \text{ eV} \cdot \text{nm}$ gives

$$\Delta E = \frac{(1240 \text{ eV} \cdot \text{nm})(0.597 \text{ nm})}{(589.592 \text{ nm})(588.995 \text{ nm})} = 2.13 \times 10^{-3} \text{ eV}$$

**Exercise 2** Using the spin–orbit interaction energy calculated in Example 8.4, deduce a value for the magnetic field strength at the site of the orbiting $3p$ electron in sodium.

**Answer**  $B = 18.38 \text{ T}$, a large field by laboratory standards.
**Bremsstrahlung**

Copper, Molydenum, ...

10–20 keV

Producing x-rays: the good old-fashioned way

+ Ze

- 1s 2p 3p e-

Line Spectra + a continuum

50–100 keV

How are these measured?

How do the 2 aspects arise?

---

Spin-orbit splitting in high-resolution x-ray spectra

2p, j = 3/2

2p, j = 1/2

Line Spectra

+a continuum

Bremsstrahlung

---

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What properties do wave functions of overlapping (thus indistinguishable) particles have?—electrons as example:

\[ \psi = \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2), \text{ including spin of both electrons} \]

But labels can't affect any measurable quantity.

E.g. — probability density:

\[ |\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)|^2 = |\psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1)|^2 \]

Therefore

\[ \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = \pm 1 \psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1) \]

\[ = \hat{P}_{12} \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) \]

with \( \hat{P}_{12} = \) permutation operator \( \rightarrow \vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2 \)

and eigenvalues of \( \pm 1 \)

Probability of finding two electrons at the same point in space with the same spin (\( \uparrow \uparrow \) or \( \downarrow \downarrow \)) is zero: “the Fermi Hole”

\( \rightarrow \) the Exchange Interaction

\( \rightarrow \) Hund’s 1st rule & magnetism
What properties do wave functions of overlapping (thus indistinguishable) particles have?—electrons as example:

\[ \psi = \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2), \text{ including spin of both electrons} \]

But labels can't affect any measurable quantity.

E.g. – probability density:

\[ |\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2)|^2 = |\psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1)|^2 \]

Therefore

\[ \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = \pm 1 \psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1) \]

\[ = \hat{P}_{12} \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) \]

with \( \hat{P}_{12} = \text{permutation operator} \rightarrow \vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2 \)

and eigenvalues of \( \pm 1 \)

Finally, all particles in two classes:

**FERMIONS** (incl. e\(^-\)'s): \( \psi \) antisymmetric

\[ s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots \]

\[ \hat{P}_{12} \psi = -1 \psi \]

**BOSONS** (incl. photons): \( \psi \) symmetric

\[ s = 0, 1, 2, \ldots \]

\[ \hat{P}_{12} \psi = +1 \psi \]

→ the Exchange Interaction
→ Hund’s 1\(^{st}\) rule & magnetism

Probability of finding two electrons at the same point in space with the same spin (\( \uparrow \uparrow \) or \( \downarrow \downarrow \)) is zero: “the Fermi Hole”
The Fermi hole or Exchange/Correlation Hole as seen in theory-silicon atom:

\[ \uparrow \uparrow \text{ or } \downarrow \downarrow \]

\[ \uparrow \downarrow \text{ or } \downarrow \uparrow \]

\[ \text{Total} \]

FIG. 1. The same spin (a), opposite spin (b) and total (c) exchange-correlation hole about a spin-up particle located at 1.4 \( a_B \) from the atom center on the \( x \) axis (parallel to the \( p \) orbitals) for the ground state of the Si atom in the \( L_z = 0 \) projection. The surface plot shows the change in density along a plane cutting through the origin along the \( x \) and \( z \) axes.

Fong (UC Davis) et al., Phys. Rev. A 62, 062507
Antisymmetry and the Pauli Exclusion Principle:

Try Helium, 2 electrons in ground state 1s wave functions, “1s²”

Simple normalized antisymmetric trial wave function is

\[ \psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = \frac{1}{\sqrt{2}} \left[ \varphi_{1s}(\vec{r}_1, \vec{s}_1 = \uparrow)\varphi_{1s}(\vec{r}_2, \vec{s}_2 = \downarrow) - \varphi_{1s}(\vec{r}_1, \vec{s}_1 = \downarrow)\varphi_{1s}(\vec{r}_2, \vec{s}_2 = \uparrow) \right] \]

Interchanging labels via permutation operator \( \hat{P}_{12} \) gives

\[ \hat{P}_{12}\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = \psi(\vec{r}_2, \vec{s}_2; \vec{r}_1, \vec{s}_1) = \frac{1}{\sqrt{2}} \left[ \varphi_{1s}(\vec{r}_2, \vec{s}_2 = \uparrow)\varphi_{1s}(\vec{r}_1, \vec{s}_1 = \downarrow) - \varphi_{1s}(\vec{r}_2, \vec{s}_2 = \downarrow)\varphi_{1s}(\vec{r}_1, \vec{s}_1 = \uparrow) \right] \]

\[ = -\psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2), \text{ as required} \]

Can’t tell which electron is spin up—indistinguishable

Also, if we try to put both electrons in 1s with spin-up (\( \uparrow \)), first term always cancels second term, and \( \psi = 0! \) Therefore, we have the Pauli Exclusion Principle !!!→

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Thus, in a many-electron system:

- Anti-symmetry of total wave function implies:

  **Pauli Exclusion Principle:**
  No two electrons can have all the same quantum nos. 
  \[ n, \ell, m_\ell, m_s \]
  or, if spin-orbit split
  \[ n, \ell, j, m_j \]

- Electronic structure determined by filling \( n, \ell \) (or \( n, \ell, j \)) levels from lowest to highest energy (\( E_{n,\ell} \) from radial Schroedinger Eqn. with \( Z_{eff} \))

- Partially filled subshells \( n, \ell \) (or \( n, \ell, j \)) have their lowest energy when a maximum no. of electrons have parallel spins = highest total spin angular momentum = \( \vec{S} \), and thus maximum avoidance (Hund’s First Rule), and then they couple to yield highest total orbital angular momentum = \( \vec{L} \) (Hund’s Second Rule)
A really accurate first wave function for He: Hylleraas, 1927-30, hand calculation and minimization of total energy:

If we take the nuclear charge to be \( +Ze \) instead of \( +2e \), we can treat helium-like ions such as \( \text{H}^- \), \( \text{Li}^+ \), \( \text{Be}^{2+} \). The Hamiltonian operator is

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}
\]

(9.49)

How can we improve our variational result? We might try a function that had the general form of (9.77), i.e., a product of two functions, one for each electron:

\[
\psi = g_1(1)g_2(2)
\]

(9.88)

However, we could try a variety of functions \( g \) in (9.88), instead of the single exponential used in (9.77). A systematic procedure for finding the function \( g \) that gives the lowest value of the variational integral will be discussed in Section 11.1. This procedure shows that for the best possible choice of \( g \) in (9.88), the variational integral equals \(-77.9\) eV, which is still in error by 1.4 percent. We might ask why (9.88) does not cause the variational integral to converge to the true ground-state energy, no matter what form we try for \( g \). The answer is that when we write the trial function as the product of separate functions for each electron, we are making an approximation. Because of the \( e^2/r_{12} \) term in the Hamiltonian, the Schroedinger equation for helium is not separable, and the true ground-state wave function cannot be written as the product of separate functions for each electron. To reach the true ground-state energy, we must go beyond a function of the form (9.88).

The Bohr model gave the correct energies for the hydrogen atom but failed when applied to helium. Hence in the early days of quantum mechanics, it was important to show that the new theory could give an accurate treatment of helium. The pioneering work on the helium ground state was done by Hylleraas in the years 1928-1930. He used variational functions that contained the interelectronic distance \( r_{12} \) explicitly. This provides an effective way of taking into account the effects of one electron on the motion of the other. One function Hylleraas used is

\[
\psi = N[e^{-\zeta r_1/\alpha_0}e^{-\zeta r_2/\alpha_0}(1 + br_{12})]
\]

(9.89)

where \( N \) is the normalization constant and \( \zeta \) and \( b \) are the variational parameters. Since

\[
r_{12} = [(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2]^{1/2}
\]

(9.90)

the function (9.89) goes beyond the simple product form (9.88). Minimization of the variational integral with respect to the parameters gives \( \zeta = 1.849, b = 0.364 \), and a ground-state energy of \(-78.7\) eV, in error by 0.3 eV. The \( 1 + br_{12} \) term makes the wave function larger for large values of \( r_{12} \); this is as it should be, because the repulsion between the electrons makes it energetically more favorable for the electrons to avoid each other. A more complicated function used by Hylleraas is

\[
\psi = e^{-\zeta r_1/\alpha_0}e^{-\zeta r_2/\alpha_0} \sum_{i,j,k} c_{ijk}(r_1 + r_2)^i(r_1 - r_2)^jr_{12}^k
\]

(9.91)

where the summation is over nonnegative integral values of \( i, j, \) and \( k \). Using a function containing six terms in the sum, Hylleraas obtained an energy only 0.01 eV above the true ground-state energy.

Hylleraas's work has been extended by others. Pekeris\(^3\) used a function of the form (9.91) containing 1078 (!) terms. The calculations involved a determinant of order 1078 and were carried out on an electronic computer. Pekeris found a ground-

---

The Hydrogenic Atom
Schroedinger Equation:
Spherical Polar Coordinates

Classically:
\[ \mathbf{L} = \mathbf{r} \times \mathbf{p} \]
\[ \tilde{L} = \mathbf{r} \times \mathbf{p} \]
is conserved
\[ \mu = \text{reduced mass} \]
\[ = \frac{m_e}{1 + \frac{m_e}{M_n}} \]

Quantum mechanically:
\[ \Psi \text{ H-ATOM SCH. EQN. IS:} \]
\[ \hat{H}\Psi(r,\theta,\phi) = \hat{K}\Psi(r,\theta,\phi) - \frac{\mathbf{e}^2}{4\pi\varepsilon_0 r} \Psi = E\Psi \]

\[ V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \]

Polar angle = \( \theta = \text{arc cos}(z/r) \)
Azimuthal angle = \( \phi = \text{arc tan}(y/x) \)

Converting to new coordinates
\[ \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi = \]
\[ -\cos \theta \int_0^r r \times 2\pi = 4\pi \]
In many-electron atoms:
For a given n, s feels nuclear charge more than p, more than d, more than f
Lifts degeneracy on ℓ in hydrogenic atom

Intraatomic electron screening in many-electron atoms--a simple model

\[ k_C = \frac{1}{(4\pi\varepsilon_0)} \]
Intraatomic electron screening in many-electron atoms—a self-consistent Q.M. calculation

Plus radial one-electron functions:

\[ P_{n\ell}(r) \equiv rR_{n\ell}(r) \]
The shell structure of an Ar atom, as measured and calculated

\[ K = L = 1s^2\ 2s^22p^6 \]

\[ M = 3s^23p^6 \]

The radial probability distribution of all of the electrons in Argon, as derived from electron diffraction experiments and quantum-mechanical theory.
Degeneracy in the hydrogenic atom with spin

<table>
<thead>
<tr>
<th>States</th>
<th>Degeneracy without spin</th>
<th>Degeneracy with spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 1$: $1s_0$</td>
<td>Not</td>
<td>2</td>
</tr>
<tr>
<td>$n = 2$: $2s_0$, $2p_{+1},2p_0,2p_{-1}$, or $2s_0, 2p_x, 2p_y, 2p_z$</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>$n = 3$: $3s_0$, $3p_x, 3p_y, 3p_z$, or $3d_{3z^2-r^2}, 3d_{x^2-y^2}, 3d_{xy}, 3d_{yz}, 3d_{xz}$</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>$n = \text{general}$</td>
<td>$n^2$</td>
<td>$2n^2$</td>
</tr>
</tbody>
</table>
Degeneracy in the a real atom with spin

<table>
<thead>
<tr>
<th>States</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 1$: $1s_0$</td>
<td>2</td>
</tr>
<tr>
<td>$n = 2$: $2s_0$</td>
<td>2</td>
</tr>
<tr>
<td>$2p_{+1}, 2p_0, 2p_{-1}$, or $2p_x, 2p_y, 2p_z$</td>
<td>6</td>
</tr>
<tr>
<td>$n = 3$: $3s_0$</td>
<td>2</td>
</tr>
<tr>
<td>$3p_x, 3p_y, 3p_z$</td>
<td>6</td>
</tr>
<tr>
<td>$3d_{3z^2-r^2}, 3d_{x^2-y^2}, 3d_{xy}, 3d_{yz}, 3d_{xz}$</td>
<td>10</td>
</tr>
<tr>
<td>$n = 4$: $4s_0$</td>
<td>2</td>
</tr>
<tr>
<td>$4p_x, 4p_y, 4p_z$</td>
<td>6</td>
</tr>
<tr>
<td>$4d_{3z^2-r^2}, 4d_{x^2-y^2}, 4d_{xy}, 4d_{yz}, 4d_{xz}$</td>
<td>10</td>
</tr>
<tr>
<td>$4f_y^3, 4f_z^3, 4f_x^3, 4f_{x(z-y)}, 4f_{y(z-x)}, 4f_{z(x-y)}, 4f_{xyz}$</td>
<td>14</td>
</tr>
<tr>
<td>$n$ total:</td>
<td>2(n^2)</td>
</tr>
</tbody>
</table>
FIGURE 7.13  The sequence of quantum states in an atom. Not to scale.
Seeing the energy levels with the photoelectric effect \( \rightarrow \) ”photoelectron spectroscopy” or “photoemission”

Gold: \( Z = 79 \):

\[
\begin{align*}
1s^2 & 2s^2 2p^6 & 3s^2 3p^6 & 3d^{10} & 4s^2 4p^6 & 4d^{10} & 4f^{14} & 5s^2 5p^6 & 5d^{10} & 6s^1
\end{align*}
\]

Electrons in Au: 5d6s

\[ h\nu = \text{Binding Energy} + \text{Kinetic Energy} \]

\[ \phi = \text{work func.} \]

\( \text{Vacuum}\) Least tightly bound

\( \text{Metal Surface} \)

Distance

\( h\nu = \text{Binding Energy} \)

Kinetic Energy

\( \text{Spin-orbit splittings} \)

\( \text{No. of photoelectrons} \)
Bremsstrahlung
Copper, Molyddenum,..
10-20 keV
Producing x-rays:
the good 
old-fashioned way
+Ze
1s
2p
3p e-
Line
Spectra
+a continuum
50-100 keV
How are these
measured?
How do the
2 aspects arise?

Hole

(2 e⁻) → (1 e⁻ with hole)

Line Spectra
+a continuum

Bremsstrahlung

\[\Delta L = -1\]
Why lines?

Why similar systematics to hydrogen, but with $Z_{\text{eff}}$?

$Z_{\text{eff}} = Z - \text{no. inner } e^- \text{-screening} \approx Z - 7 - 2 = Z - 9$ (roughly correct)

$Z_{\text{eff}} = Z - \text{no. inner } e^- \text{-screening} \approx Z - 1$

Understood now!

Square root of x-ray frequency
Filling the Atomic Orbitals:

Maximum Occupation = Degeneracy

2

1s
\( n=1 \) \( l=0 \)

2s
\( n=2 \) \( l=0 \)

2p
\( n=2 \) \( l=1 \)

3s
\( n=3 \) \( l=0 \)

3p
\( n=3 \) \( l=1 \)

3d
\( n=3 \) \( l=2 \)

+ 14 for nf
FIGURE 7.13 The sequence of quantum states in an atom. Not to scale.
Hund’s First Rule: highest total spin angular momentum
# Transition Metals

## Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters $s$, $p$, $d$, ... signify electrons having orbital angular momentum $0$, $1$, $2$, ... in units $\hbar$; the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

### Electronic Configurations

- **$s^1$**: Lanthanides, Actinides
- **$s^2$**: helium
- **$s^2\,p^6$**: noble gases
- **$s^2\,p^6\,d^{10}$**: transition metals

### Exceptions
- **d⁵ + d¹⁰**: half-filled/filled more stable
- **f⁷**: exceptions
- **f⁷**: exceptions

### LA Series
- **La**: $4f^¹ 

### Inner Transition Elements
- **Ce**: $4f^²
- **Pr**: $4f^³
- **Nd**: $4f^⁴
- **Pm**: $4f^⁵
- **Sm**: $4f^⁶
- **Eu**: $4f^⁷
- **Gd**: $4f^⁸
- **Tb**: $4f^⁹
- **Dy**: $4f^{10}
- **Ho**: $4f^{11}
- **Er**: $4f^{12}
- **Tm**: $4f^{13}
- **Yb**: $4f^{14}
- **Lu**: $4f^{15}

### Actinides
- **Ac**: $5f^¹

### Rare Earths
- **RE**: $4f^{14} 

---

**Note:** The periodic table is a visual representation of the elements, showing their atomic numbers, electron configurations, and some of their properties.
SOME PERIODIC PROPERTIES:
(plus see www.webelements.com)
From www.webelements.com, with much more: