

Lecture 16, February 24, 2006**Solved Homework** (*Homework for grading is also due today*)

Given that for a hydrogenic atom

$$\begin{aligned}\langle H \rangle &= \langle T \rangle + \langle V \rangle \\ &= \left\langle -\frac{1}{2} \nabla^2 \right\rangle - Z \langle r^{-1} \rangle\end{aligned}$$

where we have explicitly written the proper kinetic and potential energy operators. We are reminded/given that

$$\langle H \rangle = -\frac{Z^2}{2n^2} \quad \text{and} \quad \langle r^{-1} \rangle = \frac{Z}{n^2}$$

so it is trivial to determine

$$\langle T \rangle = \frac{Z^2}{2n^2}$$

Thus, the expectation value of the kinetic energy is $-1/2$ times the expectation value of the potential energy. This relationship of $\langle T \rangle = -(1/2)\langle V \rangle$ is a manifestation of what is known as the quantum mechanical virial theorem, and it holds true for *all* wave functions where the potential energy term in the Hamiltonian operator depends only on r^{-1} to one or more nuclei.

Atomic Spectroscopy

The hydrogenic (one-electron) atom has 3 quantum numbers associated with each wave function. Two of these are from the spherical harmonics, and we already know the selection rules on the spherical harmonics:

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta m_l = 0, \pm 1 \quad (16-1)$$

without derivation we will simply accept that the selection rule for Δn is that absorption/emission is allowed for *any* change in n (note that n must change from one

value to another, or else E , which depends only on n , fails to change, and then there is no opportunity to absorb or emit a photon in the first place!)

The figure on the next page illustrates allowed transitions in the spectrum of a hydrogenic atom. Note that, although the figure is terribly complicated in the sense that many, many transitions are allowed, an actual measured spectrum would be relatively simple, because of the very small number of different ΔE values. A single photon frequency is associated with each ΔE , and thus there is a single ν for every $n = 1 \rightarrow n = 2$ transition, and a single ν for every $n = 2 \rightarrow n = 3$ transition, irrespective of the actual orbitals involved at the particular principal quantum number level.

Truth is, of course, life is not quite that simple. It's only that simple if you use a low-resolution spectrometer. If you look more carefully, or you make the experiment a bit more complicated, suddenly you find a lot of new lines in the spectrum (different photon frequencies). Let's start with the most profound complication.

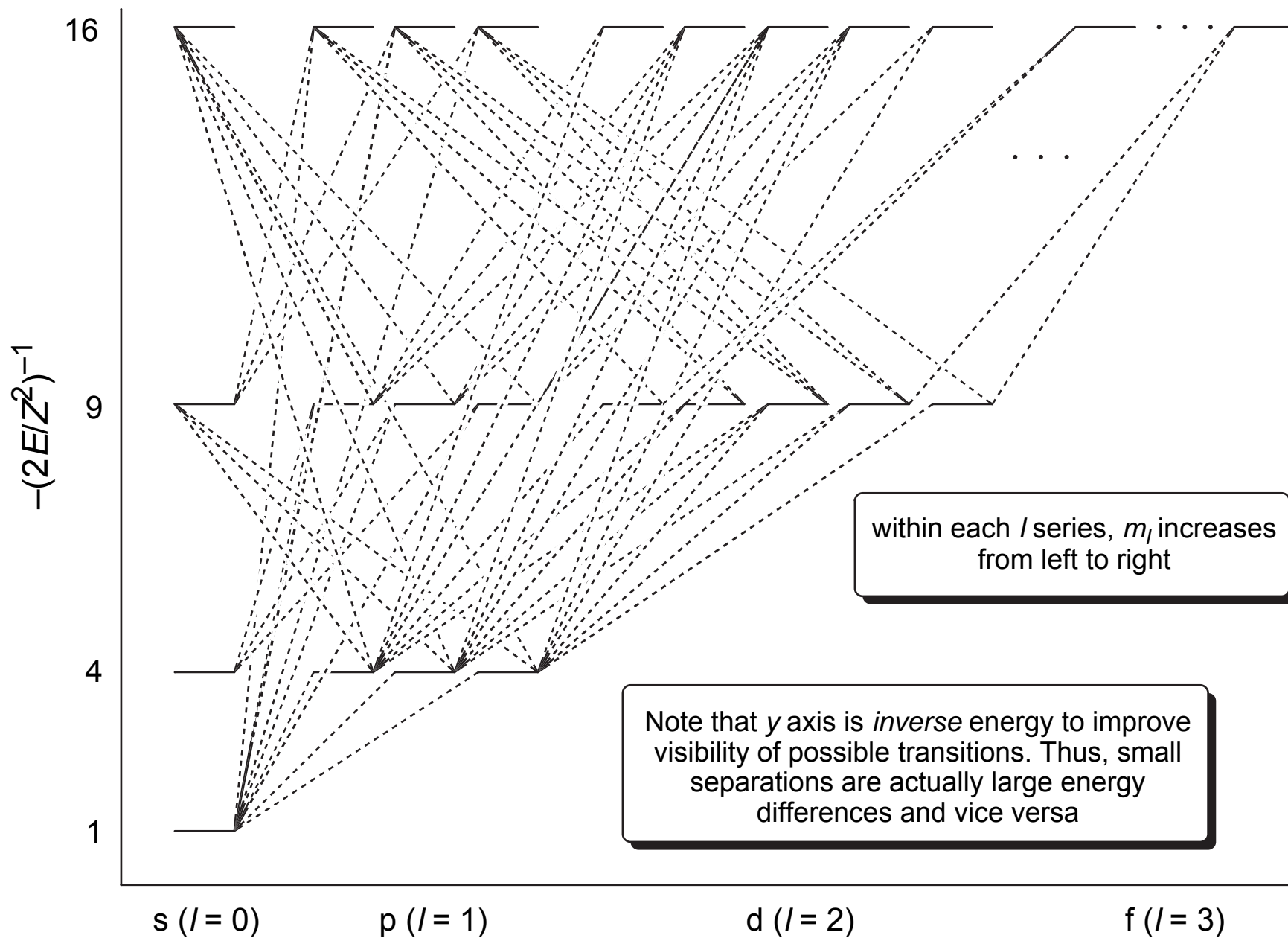
Electron Spin

In 1922, Stern and Gerlach did the following experiment.

- 1) Heat a block of silver until it vaporizes (whoa...)
- 2) Arrange the pressure in the experimental system such that the gas of silver atoms collimates into a "beam" that passes through the poles of a magnet.
- 3) Observe where the silver atoms strike a target behind the magnet.

Here's what Stern and Gerlach expected. The silver atom can be thought of as being like a very big hydrogen atom. That's because all of the electrons but one completely fill principal quantum number levels 1 to 3 and the 4s, 4p, and 4d levels. So, for the one remaining electron in the 5s orbital, it's a little bit like being around a nucleus of unit positive charge since "underneath" it, it sees 47 protons and 46 electrons that are spherically symmetric. With that picture, it should be clear that the total angular momentum of the electron/"nucleus" system is $\mathbf{L} = \mathbf{0}$, just as is the case for an H atom with its one electron in an s orbital. In the absence of angular momentum, the silver atom should not interact with a magnetic field, and the target should show a continuous smear of silver that drops off from the center, with the smearing attributable only to the beam not being perfectly collimated.

Here, though, is what they *actually* saw. Well, legend has it that Gerlach, who was doing the experiment, didn't see anything at all at first. The beam of silver atoms was so dilute that when the silver recondensed on the target there was too little to make out with the naked eye. Then Stern, the German überprofessor, came in smoking an enormous cigar, as was his wont. He leaned over the experimental apparatus, exhaled, looked at the target,



and saw *two distinct* dark lines, one above and one below. Gerlach rubbed his eyes and shook his head, and Stern walked away muttering about his collaborator's incompetence. Gerlach returned his attention to the apparatus, but the lines were gone! He called Stern again. Again, Stern came in, puffed out some cigar smoke, and pointed out the obvious dark lines.

It turns out that the silver reacted with the cigar smoke to form silver sulfide, which is a very dark opaque substance, and this permitted the visualization of the small amount of silver.

In any case, the key experimental result was that instead of a single smear of atoms, reflecting zero electronic angular momentum, there were two distinct lines, evidently reflecting some *other* angular momentum and, moreover, since the lines were distinct, that other angular momentum must be quantized, with only two possible values.

Since Stern and Gerlach knew the angular momentum couldn't come from the electron's orbital, they proposed that perhaps the electron itself was spinning about an axis, which would then introduce an angular momentum intrinsic to the electron and not associated with the orbital. Moreover, apparently the electron could spin at only one "speed", since then the two lines would be explained by spinning either clockwise or counterclockwise. Of course, they knew that electrons were quantum species, and not little spinning particles, but the terminology made a connection to classical physics and it has persisted to this day.

So, where does this intrinsic electronic "spin" come from? Well, we have to go back to Einstein again to explain it. Einstein's theory of relativity says that most of classical physics is a special case of things simplifying because the objects in which we are interested move much, much more slowly than the speed of light in a vacuum (3×10^{10} cm s⁻¹). However, as things begin to approach that limiting speed, odd things begin to happen: mass increases, length decreases, the rate of time's passage changes (ulp!), and things just get decidedly non-classical.

In 1928, Paul Dirac decided to reformulate the Schrödinger equation for a free electron in order to make it consistent with relativity. The math associated with this equation is, frankly, horrifying. Dirac, however, was as smart a mathematician as anyone could really hope to be, so, at the tender age of a typical college student, he worked out the appropriate solutions to the Schrödinger equation and discovered the startling implications of including relativity:

- 1) Positrons (the anti-particle to the electron) must exist. Actually, Dirac's math showed this, but in the end he was afraid to propose something so loony. Fifteen years later, more or less, the positron was identified after others had pointed out that his equations predicted its existence. When asked why he had not emphasized in 1928 that his theory made this prediction, he replied "Cowardice."

- 2) (This discovery is more important for us) The electron has associated with it its own quantum number s ; Dirac maintained the Stern-Gerlach nomenclature and called it the spin quantum number. The electron has an intrinsic total angular momentum of $\sqrt{3}/4\hbar$, which corresponds to a value for s of $1/2$ (remember when we explored the properties of the raising and lowering operators for angular momentum, we found that we could have either integer or half-integer solutions to the quantum numbers? We later discovered that for rotation in 3 dimensions we needed to use the integer solutions to satisfy rotational boundary conditions on ϕ , but the electron spin is a case where half-integer solutions work instead).

So, by analogy to orbital angular momentum, we have the following relationships for electronic spin angular momentum and eigenfunctions Φ :

$$S = S_x + S_y + S_z \quad (16-2)$$

and, for an odd number of electrons,

$$\begin{aligned} S^2\Phi &= s(s+1)\hbar^2\Phi \quad s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \\ S_z\Phi &= m_s\hbar\Phi \quad m_s = -s, -(s-1), \dots, -\frac{1}{2}, \frac{1}{2}, \dots, (s-1), s \end{aligned} \quad (16-3)$$

while for an even number of electrons

$$\begin{aligned} S^2\Phi &= s(s+1)\hbar^2\Phi \quad s = 0, 1, 2, \dots \\ S_z\Phi &= m_s\hbar\Phi \quad m_s = -s, -(s-1), \dots, 0, \dots, (s-1), s \end{aligned} \quad (16-4)$$

For a *single* electron, s is $1/2$, and m_s is perforce either $1/2$ or $-1/2$. When there is more than one electron, s is determined from the sum of the individual s values, just as net angular momentum is the sum of orbital angular momenta. So, two electrons can have $s = 0$ (opposite spins) or $s = 1$, and so forth.

Because there are only two eigenfunctions of the operator S_z for a single electron, these eigenfunctions have been given special names: α and β . They are defined as

$$\begin{aligned} S_z\alpha &= \frac{1}{2}\hbar\alpha \\ S_z\beta &= -\frac{1}{2}\hbar\beta \end{aligned} \quad (16-5)$$

An important thing to keep in mind is that the operators S^2 and S_z do *not* operate on functions of position or momentum, they operate on their own special sets of coordinates, called spin coordinates, which are often written as ω_n where ω means a spin coordinate and it is the coordinate for electron n . We make this point because, continuing the

notation above, we can construct a complete wave function for an electron in an atom fairly simply, noting the separability of the spatial and spin coordinates as

$$\Phi(r, \theta, \phi, \omega) = \begin{cases} \Psi(r, \theta, \phi)\alpha(\omega) \\ \text{or} \\ \Psi(r, \theta, \phi)\beta(\omega) \end{cases} \quad (16-6)$$

That is, the full wave function is just the spatial part we've already worked out times the spin part.

That's actually an approximation that works very well, generally. The truth is, however, that as of today no one has figured out how to solve the relativistic Schrödinger equation for more than one particle (e.g., not even for the hydrogen atom). Dirac won the Nobel prize for his work on the electron; he was so young that his mother had to chaperone him to Stockholm to accept it.

Total Angular Momentum

The total angular momentum of an electron is defined as \mathbf{J} and is, to a good approximation in light atoms (through about the first five rows of the periodic table), equal to $\mathbf{L} + \mathbf{S}$. So, if we think of an electron in an s orbital, $l = 0$ and $s = 1/2$, and thus $j = 1/2$ (j is the quantum number for the operator \mathbf{J}). If the electron is in a p orbital, $l = 1$. However, \mathbf{L} and \mathbf{S} are vector quantities, so when we add them we need to worry about whether they add cooperatively or anticooperatively. If they add cooperatively, $j = 3/2$, if anticooperatively, $j = 1/2$. For a d orbital, we have possible j values of $5/2$ and $3/2$, and so on.

For a hydrogenic atom, we write the precise one-electron wave function as follows

$$\Psi = \begin{cases} n^2 S_j & \text{when } l = 0, j = 1/2 \\ \text{or} \\ n^2 P_j & \text{when } l = 1, j = 1/2, 3/2 \\ \text{or} \\ n^2 D_j & \text{when } l = 2, j = 3/2, 5/2 \\ \text{or} \\ n^2 F_j & \text{when } l = 3, j = 5/2, 7/2 \\ \text{etc.} \end{cases} \quad (16-7)$$

where n specifies the principle quantum number (1, 2, 3, etc.), S, P, D , etc. are upper-case letters specifying the value of l (by analogy to the orbitals with corresponding lower-case letters). The "2" is a left-superscript of the upper-case letter and is pronounced "doublet". We'll say more about this when we start dealing with systems having more than one electron. The subscript can take on one of two values, as indicated.

It turns out that states of identical n and l but different j have different energies. The energy difference is equal to

$$\Delta E_{j+1,j} = A_{nl}(j+1) \quad (16-8)$$

where the "spin-orbit coupling constant" is defined in atomic units as

$$A_{nl} = \frac{\alpha^2}{2} \frac{Z^4}{n^3 l(l+1/2)(l+1)} \quad (16-9)$$

where α is called the "fine-structure constant" and is equal to $1/c$ where c is the speed of light (in atomic units), Z is the atomic number, and n and l are the principal and azimuthal quantum numbers. For the 2^2P state of hydrogen, A_{21} is about $0.000001 E_h$. This energy difference between the $1/2$ and $3/2$ j states is very small: roughly 0.4 cm^{-1} . Thus, it is difficult to see the two energy levels without a very high resolution spectrometer (the transition itself is at $82,260 \text{ cm}^{-1}$, so the splitting is 0.0005% of the transition energy). Note, however, that the size of the spin-orbit coupling constant depends on the 4th power of the atomic number. So, by the time one gets to fairly heavy atoms, say, $Z = 50$, the numerator is 6,250,000 times larger. The denominator is also slightly larger, since the principal quantum numbers for valence orbitals go up too, but the splitting can become quite noticeable on a "chemical" scale.

It is worth noting that the spectroscopy of the atom has a selection rule for j as well as for l and m_j . That rule is $\Delta j = 0$ or ± 1 .

The Zeeman Effect and Electron Spin Resonance Spectroscopy

In the presence of a magnetic field (as in the Stern-Gerlach experiment), the magnetic moment associated with a charged particle like an electron possessing angular momentum can interact with the magnetic field. When the moment is aligned with the field, energy is higher than when it opposes the field. A more formal way to express this is to say that the Hamiltonian operator changes when there is a magnetic field. In addition to the kinetic energy and Coulomb potential terms, there is a new term involving the magnetic field, so that the total energy E is now computed as

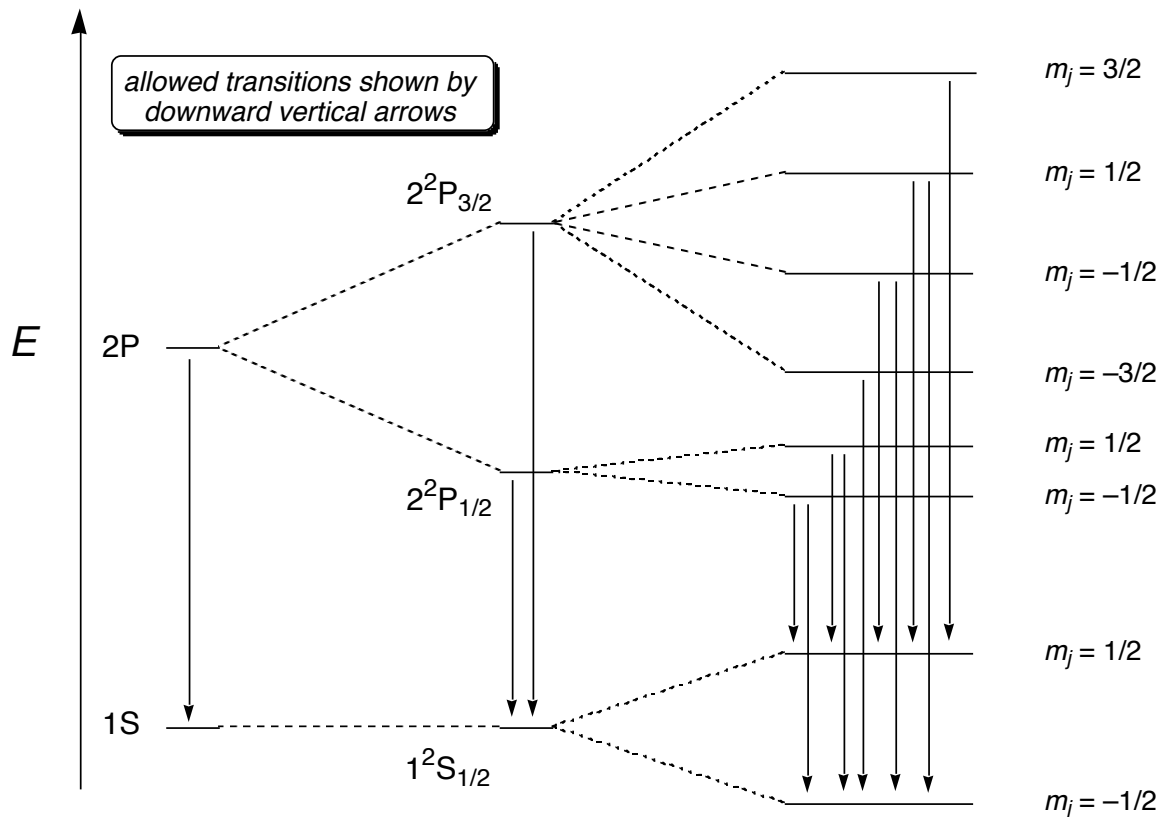
$$E = T + V + g_j \mu_B H m_j \quad (16-10)$$

where μ_B is the Bohr magneton, which is the magnetic moment of a free electron (it is equivalent to the gyromagnetic ratio in nuclear magnetic resonance (NMR) spectroscopy of nuclei), H is the magnetic field strength, m_j is the quantum number for the component of the total angular momentum \mathbf{J} along the magnetic field direction (nearly always called the z direction), and g_j is called the Landé g factor. The g factor is much like the chemical shift in NMR spectroscopy: it provides information about the "environment" of the electron. For a free electron, it is very close to 2.0. In an atom, it is equal to

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad (16-11)$$

where j , s , and l are the total angular momentum, spin, and azimuthal quantum numbers, respectively. (Notice that for a free electron we'd expect $s = 1/2$, and $j = 1/2$, and perhaps $l = 0$ since the electron is not in an orbital but is a delocalized sine or cosine wave, so the quoted value of about 2.0 for the free electron is consistent with equation 16-11.)

Recalling that m_j can take on half integer values ranging from $-j$ to j , this implies that a magnetic field will "split the degeneracy" of levels characterized by a single j value. Thus, a particular j level will split into its various m_j energy levels, each of which is separated from the next by $g_j\mu_B H$. This splitting is known as the Zeeman effect. The selection rule that comes into play after this splitting allows only transitions for which



$\Delta m_j = 0$ or ± 1 . The figure above illustrates the energy levels involved in our various models for the H atom.

On the left are the 1S and 2P energy levels for the "spin-free" hydrogen atom (a fictional system). When electron spin is considered, the 2P level splits into $j = 1/2$ and $3/2$ levels, and the splitting depends on the spin orbit coupling constant as discussed above. There are two allowed transitions in this system compared to the spin-free case. This is the situation that is observed in actual H in the *absence* of an applied magnetic field. When a magnetic field *is* applied, *all* levels are split into their various m_j energy levels, with the splitting dependent on the electronic g value and the strength of the applied magnetic field. For the same electronic states there are now *ten* allowed transitions.

In addition to the Zeeman effect on electronic spectroscopy (which is typically carried out in the visible/UV range of the spectrum), a different spectroscopic technique called electron spin resonance spectroscopy, or ESR, can measure directly transitions between different m_j energy levels for a single state (for typical magnetic fields, such transitions occur in the microwave region of the spectrum). This permits determination of g which is to ESR what the chemical shift δ is to NMR. Since g tells about the nature of the orbital in which a free electron resides, it can offer much chemical insight into the nature of systems having unpaired electrons. One of the first ESR spectra was of the unpaired electron in chlorophyll which aided in the explanation of the mechanism of photosynthesis in green plants.

Homework (n/a — prepare for Exam II)

Sample Exam Problems

- Which of the following statements is/are true about $\langle x^2 \rangle$ evaluated for one-dimensional QMHO wave functions over the same potential V ?

(a) Parity requires it to be zero for levels where n is even (b) It decreases with increasing n (c) It is equal to $\langle x \rangle^2$ (d) It is always positive	(e) It is equal to $\langle V \rangle / k$ where k is the oscillator force constant (f) (b) and (c) (g) (c) and (d) (h) (b), (d), and (e)
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2. Which of the following statements about angular momentum operators, eigenvalues, and eigenfunctions is/are *true*?

- | | |
|---|-----------------------|
| (a) $L_+ = (L_-)^*$ | (e) $L_- Y_{l,l} = 0$ |
| (b) $\langle L^2 \rangle = \langle L_z \rangle^2$ if $m_l = l$ | (f) (a) and (e) |
| (c) For each value of l there are $2l + 1$ possible values of m_l | (g) (a), (c) and (d) |
| (d) $L_+ Y_{l,l} = 0$ | (h) All of the above |

3. For a diatomic molecule, what is the rotational constant B ?

- | | |
|-----------------------------|--|
| (a) The eigenvalue of L^2 | (e) $\hbar^2 / \mu R^2$ where μ is the reduced mass and R is the bond length |
| (b) The eigenvalue of L_z | (f) $\hbar^2 / 2I$ where I is the moment of inertia |
| (c) 0 | (g) (e) and (f) |
| (d) $J + K$ | (h) None of the above |

4. An electron of spin α is in a 3d orbital. Which of the below sets of quantum numbers ($n, l, m_l, s, m_s, j, m_j$) might reasonably describe such an electron?

- | | |
|--------------------------------------|-----------------------------------|
| (a) (3, 3, 3, 3, 3, 3, 1) | (e) (3, 2, 2, 1/2, 1/2, 5/2, 5/2) |
| (b) (3, 3, 2, 1/2, 1/2, 5/2, 5/2) | (f) (c) and (e) |
| (c) (3, 2, 0, 1/2, 1/2, 5/2, 1/2) | (g) (b), (c), (d) and (e) |
| (d) (3, 2, 0, -1/2, -1/2, 5/2, -1/2) | (h) None of the above |

(Answers may be found on class website)