

## IV. Electronic Spectroscopy, Angular Momentum, and Magnetic Resonance

The foundation of electronic spectroscopy is the exact solution of the time-independent Schrodinger equation for the hydrogen atom. This is the only atomic or molecular system for which there is an exact solution.

In section I, the Bohr model of the hydrogen atom yielded correct energies with correlation of energy levels with the  $z$ -component of electronic orbital angular momentum. Greater angular momentum correlated with higher energy.

The potential energy contribution to the Hamiltonian is the Coulombic interaction  $-(1/4\pi\epsilon_0)(e^2/r)$ . Polar coordinates  $(r, \theta, \phi)$  are good for the hydrogen atom Schrodinger equation because the potential is radial:

$$(2mr^2)^{-1} \{ -\hbar^2 [d/dr(r^2 d\psi/dr)] - \hbar^2 [(1/\sin\theta) d/d\theta(\sin\theta d\psi/d\theta)] - \hbar^2 [(1/\sin^2\theta) d^2\psi/d\phi^2] \} - (1/4\pi\epsilon_0)(e^2/r)\psi = E\psi \quad (\text{IV.1})$$

The kinetic energy term in braces is split between the first term which only contains derivatives with respect to  $r$  and the second two terms which contain derivatives with respect to  $\theta, \phi$ . These second two terms are the squared angular momentum of the electron:

$$(2mr^2)^{-1} \{ [(-\hbar^2)d/dr(r^2 d\psi/dr)] + L^2\psi \} - (1/4\pi\epsilon_0)(e^2/r)\psi = E\psi \quad (\text{IV.2})$$

$$L^2 = \mathbf{L} \cdot \mathbf{L} = (\mathbf{r} \times \mathbf{p}) \cdot (\mathbf{r} \times \mathbf{p}) \quad (\text{IV.3})$$

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = (x\mathbf{x} + y\mathbf{y} + z\mathbf{z}) \times -i\hbar \{ (d/dx)\mathbf{x} + (d/dy)\mathbf{y} + (d/dz)\mathbf{z} \} \quad (\text{IV.4})$$

$L^2$  can be written in spherical polar coordinates using the following equations:

$$x = r \sin\theta \cos\phi \quad (\text{IV.5})$$

$$y = r \sin\theta \sin\phi \quad (\text{IV.6})$$

$$z = r \cos\theta \quad (\text{IV.7})$$

In Eq. IV.2, the kinetic energy operator  $L^2/2mr^2$  corresponds to the kinetic energy operator for an electron moving on a sphere of radius  $r$ . This operator is analogous to the kinetic energy operator of the radial atom Hamiltonian (Eq. II.39). The other kinetic energy operator in Eq. IV.2 corresponds to kinetic energy along the  $r$  direction.

Eq. IV.2 is solved by separation of variables:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad (\text{IV.8})$$

$$(2mr^2)^{-1} \{ [(-\hbar^2 Y) d/dr(r^2 dR/dr)] + RL^2 Y \} - (1/4\pi\epsilon_0)(e^2/r)RY = E(RY) \quad (\text{IV.9})$$

Note that  $L^2$  operates on  $Y$  which includes taking derivatives. Multiply Eq. IV.9 by  $2mr^2/(RY)$ :

$$(-\hbar^2/R)d/dr(r^2dR/dr) - (1/4\pi\epsilon_0)(2mre^2) - 2mr^2E + L^2Y/Y = 0 \quad (\text{IV.10})$$

The first three terms depend only on  $r$  while the last term depends only on  $\theta$  and  $\phi$ . Eq. (IV.10) is only possible for all  $r, \theta, \phi$  when the sum of the first three terms is equal to a constant and the last term is equal to  $-1$  times that constant. With foresight, the constant is called  $-l(l+1)\hbar^2$  so that an equation can be written for the last term:

$$L^2(Y) = l(l+1)\hbar^2Y \quad (\text{IV.11})$$

Consider:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \quad (\text{IV.12})$$

Eq. IV.12 is rewritten using the expression for  $L^2$  from Eq. IV.1:

$$-\hbar^2\left\{[(1/\sin\theta) d/d\theta(\sin\theta d(\Theta\Phi)/d\theta)] + [(1/\sin^2\theta) d^2(\Theta\Phi)/d\phi^2]\right\} = l(l+1)\hbar^2(\Theta\Phi) \quad (\text{IV.13})$$

Multiply Eq. IV.13 by  $-\sin^2\theta/(\Theta\Phi)$ :

$$\hbar^2(\sin\theta/\Theta) d/d\theta(\sin\theta d\Theta/d\theta) + l(l+1)\hbar^2\sin^2\theta + \hbar^2(1/\Phi) d^2\Phi/d\phi^2 = 0 \quad (\text{IV.14})$$

The first two terms depend only on  $\theta$  and the last term depends only on  $\phi$ . In order for the sum to be 0 for all  $\theta, \phi$ , the first two terms and last term must be constants with opposite sign. Set the constants as  $m^2\hbar^2$  and  $-m^2\hbar^2$ . For the third term:

$$\hbar^2 d^2\Phi/d\phi^2 = -m^2\hbar^2 \Phi \quad (\text{IV.15})$$

$$(-i\hbar d/d\phi)^2 \Phi = m^2\hbar^2 \Phi \quad (\text{IV.16})$$

$$L_z^2 \Phi = m^2\hbar^2 \Phi \quad (\text{IV.17})$$

The eigenvalues and eigenfunctions for this equation are taken from Eqs. II.25 and II.41.

$$\Phi_m(\phi) = (2\pi)^{-1/2} e^{im\phi}, \quad m = \text{integer} \quad (\text{IV.18})$$

These are the eigenfunctions of the angular momentum along the  $z$  direction. The eigenvalue for the projection of rotational angular momentum on the space-fixed  $z$  axis is  $m\hbar$ . This is the only cartesian projection of angular momentum which we know with certainty.

The  $\Theta$  eigenfunctions are the *Legendre polynomials* and are functions of  $\cos\theta$ :

$$\Theta_{lm} = P_l^{|m|}(\cos\theta) \quad l, m \text{ are integers with } l \geq 0 \quad (\text{IV.19})$$

$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$  are known as the *spherical harmonics* and a few representative normalized  $Y_{lm}$  are presented:

$$\begin{aligned} |Y_{00}\rangle &= (1/4\pi)^{1/2} \\ |Y_{10}\rangle &= (3/4\pi)^{1/2} \cos\theta \\ |Y_{1\pm 1}\rangle &= \mp (3/8\pi)^{1/2} \sin\theta e^{\pm i\phi} \\ |Y_{20}\rangle &= (5/16\pi)^{1/2} (3\cos^2\theta - 1) \\ |Y_{2\pm 1}\rangle &= \mp (15/8\pi)^{1/2} \cos\theta \sin\theta e^{\pm i\phi} \\ |Y_{2\pm 2}\rangle &= (15/32\pi)^{1/2} \sin^2\theta e^{\pm 2i\phi} \end{aligned} \quad (\text{IV.20})$$

Note:

$$L^2 |Y_{lm}\rangle = l(l+1)\hbar^2 |Y_{lm}\rangle \quad (\text{IV.21})$$

$$L_z |Y_{lm}\rangle = m\hbar |Y_{lm}\rangle \quad (\text{IV.22})$$

$$L_z^2 |Y_{lm}\rangle = m^2\hbar^2 |Y_{lm}\rangle \quad (\text{IV.23})$$

Note that  $\langle L_z^2 \rangle \leq \langle L^2 \rangle$  because the magnitude of angular momentum along one axis cannot be greater than the total magnitude of angular momentum. This physical limitation leads to the restriction  $|m| \leq l$ . For example, for  $l = 2$ ,  $m = -2, -1, 0, 1, 2$ .

$Y_{lm}$  are commonly denoted by letters with  $l = 0, 1, 2, 3$  referred to as *s, p, d, and f* orbitals.

The *parity* or space inversion of  $Y_{lm}$  has a  $(-1)^l$  dependence. The parity operation is described in cartesian coordinates by the operation  $x \rightarrow -x, y \rightarrow -y, z \rightarrow -z$  or  $\mathbf{r} \rightarrow -\mathbf{r}$ . In polar coordinates, the parity operation is described by  $\theta \rightarrow \pi - \theta, \phi \rightarrow \phi + \pi$  and:

$$Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi) \quad (\text{IV.24})$$

The  $Y_{lm}$  with even  $l$  have even parity and the  $Y_{lm}$  with odd  $l$  have odd parity. The even parity  $Y_{lm}$  do not change with coordinate inversion while the odd parity  $Y_{lm}$  change sign with space inversion.

The parity of the  $Y_{lm}$  can be useful in calculating integrals over the angular  $\theta, \phi$  coordinates. An integral can only be non-zero if the parity of the total product of the wavefunctions and the

operator function is even. For two functions, odd  $\times$  odd = even, even  $\times$  even = even, and even  $\times$  odd = odd.

Consider the dipole selection rules for transition intensities between different  $RY_{lm}$  (Eq. III.21):

$$I \propto |\langle RY_{l_2m_2} | \mu_x | RY_{l_1m_1} \rangle|^2 \epsilon_x^2 + |\langle RY_{l_2m_2} | \mu_y | RY_{l_1m_1} \rangle|^2 \epsilon_y^2 + |\langle RY_{l_2m_2} | \mu_z | RY_{l_1m_1} \rangle|^2 \epsilon_z^2 \quad (\text{IV.25})$$

$$\langle RY_{l_2m_2} | \mu_x | RY_{l_1m_1} \rangle = -\langle RY_{l_2m_2} | er \sin \theta \cos \phi | RY_{l_1m_1} \rangle = -\langle R | er | R \rangle \langle Y_{l_2m_2} | \sin \theta \cos \phi | Y_{l_1m_1} \rangle \quad (\text{IV.26})$$

$$\langle RY_{l_2m_2} | \mu_y | RY_{l_1m_1} \rangle = -\langle RY_{l_2m_2} | er \sin \theta \sin \phi | RY_{l_1m_1} \rangle = -\langle R | er | R \rangle \langle Y_{l_2m_2} | \sin \theta \sin \phi | Y_{l_1m_1} \rangle \quad (\text{IV.27})$$

$$\langle RY_{l_2m_2} | \mu_z | RY_{l_1m_1} \rangle = -\langle RY_{l_2m_2} | \cos \theta | RY_{l_1m_1} \rangle = -\langle R | er | R \rangle \langle Y_{l_2m_2} | \cos \theta | Y_{l_1m_1} \rangle \quad (\text{IV.28})$$

The integrals in Eqs. IV.26-28 are separated into  $r$  and  $\theta, \phi$  integrals. The dipole moment operator  $\boldsymbol{\mu} = -e\mathbf{r}$  and its three components  $\mu_x, \mu_y,$  and  $\mu_z$  have odd parity and one dipole selection rule is that transitions only occur between  $Y_{lm}$  with opposite parity. This is shown by Eqs. IV.26-28. Further analysis shows there are only non-zero transition dipole moments for  $\Delta l = \pm 1$ .

The  $m$  selection rule can be derived from considering only the  $\phi$  part of the transition dipole moment integrals. For the  $\mu_x$  component for a  $m_2 \leftarrow m_1$  transition:

$$\begin{aligned} \int_0^{2\pi} \Phi_{m_2}^* \cos \phi \Phi_{m_1} d\phi &= (2\pi)^{-1} \int_0^{2\pi} e^{-im_2\phi} \cos \phi e^{im_1\phi} d\phi = \\ (4\pi)^{-1} \{ \int_0^{2\pi} e^{-im_2\phi} e^{i\phi} e^{im_1\phi} d\phi + \int_0^{2\pi} e^{-im_2\phi} e^{-i\phi} e^{im_1\phi} d\phi \} &= \\ (4\pi)^{-1} \{ \int_0^{2\pi} e^{i(m_1 - m_2 + 1)\phi} d\phi + \int_0^{2\pi} e^{i(m_1 - m_2 - 1)\phi} d\phi \} & \quad (\text{IV.29}) \end{aligned}$$

Each integral is only non-zero if the argument of the exponential is 0 and results in a  $\Delta m = \pm 1$  selection rule. Analysis of the  $\mu_y$  component also results in a  $\Delta m = \pm 1$  selection rule and analysis of the  $\mu_z$  component results in a  $\Delta m = 0$  selection rule. The overall  $m$  selection rule is then  $\Delta m = 0, \pm 1$ .

## Magnetic Resonance

Much of the quantum mechanics of angular momentum described for the electron can be directly applied to nuclear and electron spin magnetic resonance. Recall Eqs. I.2.23 and I.2.24 for the spin magnetic moment:

$$\boldsymbol{\mu} = \gamma \mathbf{L} = \gamma \hbar \mathbf{S} = \gamma \hbar (S_x \mathbf{x} + S_y \mathbf{y} + S_z \mathbf{z}) \quad (\text{IV.30})$$

$\mathbf{S} = \mathbf{L}/\hbar$  is the “spin operator” and is unitless. Assuming that Eqs. IV.21 and IV.22 are general for any angular momentum:

$$S^2 |S, m\rangle = L^2/\hbar^2 |S, m\rangle = S(S+1) |S, m\rangle \quad (\text{IV.31})$$

$$S_z |S, m\rangle = m |S, m\rangle \quad (\text{IV.32})$$

There is a confusing convention that “ $S$ ” refers both to the spin operator and to the spin quantum number  $S \equiv l$ .

Unlike the orbital angular momentum of the electron which can have any integral  $l \geq 0$ ,  $S$  has a single integer or half-integer value specific to the electron or particular nuclear isotope. For example,  $S = 1/2$  for  $e^-$ ,  $^1\text{H}$ , and  $^{13}\text{C}$ ,  $S = 1$  for  $^2\text{H}$  and  $^{14}\text{N}$ , and  $S = 3/2$  for  $^{23}\text{Na}$ . The  $|m| \leq S$  so that for  $^2\text{H}$ ,  $m = -1, 0, 1$ .

A time-independent Schrodinger Equation for magnetic resonance in an external magnetic field  $\mathbf{B}_{ext} = B_0 \mathbf{z}$  (Eq. I.2.22):

$$\mathcal{H} |S, m\rangle = \{-\boldsymbol{\mu} \cdot \mathbf{B}_{ext}\} |S, m\rangle = E_m |S, m\rangle \quad (\text{IV.33})$$

$$\{-\gamma \hbar (S_x \mathbf{x} + S_y \mathbf{y} + S_z \mathbf{z}) \cdot B_0 \mathbf{z}\} |S, m\rangle = E_m |S, m\rangle \quad (\text{IV.34})$$

$$-\gamma \hbar B_0 S_z |S, m\rangle = E_m |S, m\rangle \quad (\text{IV.35})$$

$$E_m = -\gamma \hbar B_0 m \quad (\text{IV.36})$$

Determination of selection rules is aided by raising and lowering operators:

$$S_+ = L_+/\hbar = S_x + iS_y \quad (\text{raising operator}) \quad (\text{IV.37})$$

$$S_- = L_-/\hbar = S_x - iS_y \quad (\text{lowering operator}) \quad (\text{IV.38})$$

These operators have the properties:

$$S_+ |S, m\rangle = [S(S+1) - m(m+1)]^{1/2} |S, m+1\rangle \quad (\text{IV.39})$$

$$S_- |S, m\rangle = [S(S+1) - m(m-1)]^{1/2} |S, m-1\rangle \quad (\text{IV.40})$$

The  $\mu_x$  transition dipole moment integral for the  $|S, m_2\rangle \leftarrow |S, m_1\rangle$  transition:

$$\begin{aligned} \langle S, m_2 | \mu_x | S, m_1 \rangle &= (\gamma \hbar / 2) \{ \langle S, m_2 | S_+ | S, m_1 \rangle + \langle S, m_2 | S_- | S, m_1 \rangle \} \\ &= (\gamma \hbar / 2) \{ [S(S+1) - m(m+1)]^{1/2} \langle S, m_2 | S, m_1+1 \rangle + [S(S+1) - m(m-1)]^{1/2} \langle S, m_2 | S, m_1-1 \rangle \} \end{aligned} \quad (\text{IV.41})$$

The first integral is non-zero for  $m_2 = m_1 + 1$  and the second integral is non-zero for  $m_2 = m_1 - 1$  and result in a  $\Delta m = \pm 1$  selection rule. This result is confirmed by the  $\mu_y$  and the  $\mu_z$  transition dipole moment integrals.

The magnetic resonance transition frequency:

$$\nu = \gamma B_0 / 2\pi \quad (\text{IV.42})$$

In addition to the large external field  $B_0 \mathbf{z}$ , there are smaller internal magnetic fields within the molecule that vary with chemical and geometric structure. These internal or “local” fields are different for different nuclei and electrons and determination of these fields from the magnetic resonance spectrum provides most of the chemical and structural information.

The most important internal fields are along the  $z$  direction:

$$\mathbf{B} = (B_0 + B_{int}) \mathbf{z} \quad (\text{IV.43})$$

$$\nu = (\gamma / 2\pi) (B_0 + B_{int}) \quad (\text{IV.44})$$

For nuclear spins, the most important internal fields are due to *chemical shielding*. There are electronic currents induced by the external field and the chemical shielding fields are the magnetic fields of the induced currents (see page 1). The induced currents, chemical shielding, and NMR frequency depend on the chemical bonds of the nucleus:

$$\mathbf{B}_{shield} = -\sigma B_0 \mathbf{z} \quad (\text{IV.45})$$

where  $\sigma$  is typically positive and  $10^{-6} < \sigma_{typical} < 10^{-3}$ . Note that  $\mathbf{B}_{shield}$  is typically antiparallel to  $\mathbf{B}_{ext}$  and therefore reduces  $\nu$ .

The induced currents and  $\sigma$  will also depend on the orientation of the chemical bonds in the magnetic field and this dependence is called the *chemical shielding anisotropy*.

Inclusion of  $B_{shield}$  in Eq. IV.44:

$$\nu_{shield} = \gamma \hbar B_0 (1 - \sigma) \quad (\text{IV.46})$$

Experimental determination of  $\sigma$  as defined in Eq. IV.44 is difficult because measurement of  $\nu$  in a compound with  $\sigma = 0$  corresponds to the nucleus with no electrons. It is more practical to measure  $\Delta\nu$  and therefore  $\sigma$  relative to some reference compound:

$$\Delta\nu_{shield} = -\gamma B_0\sigma/2\pi \quad (\text{IV.47})$$

$$\delta = -\sigma = 2\pi\Delta\nu_{shield}/\gamma B_0 \quad (\text{IV.48})$$

The  $\delta$  is called the *chemical shift* and is typically reported in ppm.

Another significant internal field is *scalar* or *J-coupling*:

$$\mathbf{B}_{scalar} = -(2\pi JM/\gamma) \mathbf{z} \quad (\text{IV.49})$$

$$\nu_{scalar} = JM \quad (\text{IV.50})$$

In these equations,  $M$  refers to the  $m$  value of a nearby nuclear spin which has chemical bond connectivity with the nuclear spin undergoing a transition and  $J$  is a “coupling constant” particular to the two spins and their chemical bond connectivity. For example,  $J \sim 150$  Hz for a directly bonded  $^1\text{H}$ - $^{13}\text{C}$  spin pair.

In a typical sample, the nearby spin has nearly equal probabilities of being in any of its  $M$  states. A multiplet of transitions are observed and each transition corresponds to a different  $M$  value. For example, consider detection of  $^{13}\text{C}$  in a  $^1\text{H}$ - $^{13}\text{C}$  spin pair.  $S(^1\text{H}) = 1/2$  and  $J = 150$  Hz:

$$M = 1/2 \quad \nu_{scalar} = J/2 = 75 \text{ Hz} \quad (\text{IV.51})$$

$$M = -1/2 \quad \nu_{scalar} = -J/2 = -75 \text{ Hz}$$

$$\Delta\nu_{scalar} = J = 150 \text{ Hz} \quad (\text{IV.52})$$

The scalar fields result in splittings in the spectra.

The chemical shift and scalar couplings are both sensitive to the local bonding of the nucleus and measurement of these parameters in the NMR spectrum is helpful in assignment of individual peaks to specific nuclei. Because the chemical shifts and scalar couplings of particular functional groups are well-known, NMR spectra are also very useful for determination of the chemical structures of unknown compounds.

Distinguishing between  $\Delta\nu_{shield}$  and  $\Delta\nu_{scalar}$  is most straightforwardly done by taking NMR spectra at two different  $B_0$  fields. Note that  $\Delta\nu_{shield} \propto B_0$  while  $\Delta\nu_{scalar}$  is independent of  $B_0$ .

### Return to Hydrogen Atom

The radial part of the time-independent Schrodinger equation for the hydrogen atom will now be solved. The first three terms of Eq. IV. 10:

$$(-\hbar^2/R) d/dr(r^2 dR/dr) - (1/4\pi\epsilon_0)(2mre^2) - 2mr^2E = -\hbar^2 l(l+1) \quad (\text{IV.53})$$

Multiply by  $R/2mr^2$  and rearrange terms:

$$(-\hbar^2/2mr^2) d/dr(r^2 dR/dr) + [(\hbar^2/2mr^2)l(l+1) - (1/4\pi\epsilon_0)(e^2/r)]R = ER \quad (\text{IV.54})$$

The first term in this equation is the radial kinetic energy, the second term is the *centrifugal potential*, and the third term is the Coulomb potential. The centrifugal potential reflects the “conservation” of angular momentum; i.e.  $L^2 = \hbar^2 l(l+1) \equiv \text{constant}$ . In order for  $L^2 = |\mathbf{r} \times \mathbf{p}|^2$  to be independent of  $\mathbf{r}$ ,  $p^2$  and the kinetic energy associated with angular motion (centrifugal potential) are proportional to  $r^{-2}$ . The centrifugal potential is also apparent in the classical mechanics solution of two particles with an attractive radial potential.

The  $R$  eigenfunctions are the associated Laguerre Polynomials  $R_{nl}(r)$  which are indexed by the radial or “principal” quantum number  $n$ , an integer greater to or equal to 1 and the angular momentum or “azimuthal” quantum number  $l$  with  $n > l$ ,  $l = 0 \equiv s$ ,  $l = 1 \equiv p$ ,  $l = 2 \equiv d$ .

$$1s \quad R_{10} = (a_0)^{-3/2} 2 e^{-r/a_0} \quad (\text{IV.55})$$

$$2s \quad R_{20} = (a_0)^{-3/2} (1/8)^{1/2} [2 - (r/a_0)] e^{-2r/a_0} \quad (\text{IV.56})$$

$$2p \quad R_{21} = (a_0)^{-3/2} (1/24)^{1/2} (r/a_0) e^{-2r/a_0} \quad (\text{IV.57})$$

$$3s \quad R_{30} = (a_0)^{-3/2} (1/243)^{1/2} [6 - (4r/a_0) + (4r^2/9a_0^2)] e^{-3r/a_0} \quad (\text{IV.58})$$

$$3p \quad R_{31} = (a_0)^{-3/2} (1/486)^{1/2} [4 - (2r/3a_0)] e^{-3r/a_0} \quad (\text{IV.59})$$

$$3d \quad R_{32} = (a_0)^{-3/2} (1/2430)^{1/2} (r/a_0)^2 e^{-3r/a_0} \quad (\text{IV.60})$$

The total eigenfunction:

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \quad (\text{IV.61})$$

It is interesting to calculate the integrated probability for the electron over a spherical shell of radius  $r$ . This “radial probability density” is independent of  $\theta$ ,  $\phi$  and is proportional to the surface area of the sphere =  $4\pi r^2$ :

$$(\text{Radial probability density})_{nl} \propto r^2 R_{nl}^2 \quad (\text{IV.62})$$

$$(\text{Angular probability density})_{lm} \propto Y_{lm}^2 \quad (\text{IV.63})$$



The hydrogen atom energy eigenvalues:

$$E = - (1/4\pi\epsilon_0)^2 \times (1/n^2) \times me^4/2\hbar^2 \quad (\text{IV.64})$$

This is the same solution as the Bohr atom semiclassical approach, Eq.1.2.9. Note though that the ‘ $n$ ’ in the Bohr atom is the component of angular momentum along the  $z$  axis. In the quantum mechanical solution, the Bohr atom ‘ $n$ ’ is the “magnetic” quantum number ‘ $m$ ’ whose value has no effect on the energy. In the quantum mechanical approach, the energy for a given  $n$  is independent of  $l$  and  $m$ . So, the energy (although not the wavefunction) is independent of the angular momentum. Note that as  $n$  increases,  $\langle r \rangle$  increases,  $\langle V_{coulomb} \rangle$  increases, and  $E$  increases.

Different eigenfunctions with the same energy are “degenerate”. For example,  $n = 1$  has a degeneracy of 1 ( $1s$ ),  $n = 2$  has a degeneracy of 4 ( $1s, 2p$ ), and  $n = 3$  has a degeneracy of 9 ( $3s, 3p, 3d$ ).

The selection rule for changes in the radial quantum number  $n$  are calculated from the integration over  $r$  in Eqs. IV.26-IV.28 along with incorporation of the  $\Delta l = \pm 1$  selection rule:

$$-\langle R_{n_2, l+1} | er | R_{n_1, l} \rangle \quad (\text{IV.65})$$

$$-\langle R_{n_2, l-1} | er | R_{n_1, l} \rangle \quad (\text{IV.66})$$

The radial quantum number selection rule:

$$\Delta n = \text{anything} \quad (\text{IV.67})$$

This selection rule and energy levels are consistent with the experimental hydrogen atom spectrum.

One interesting aspect of the hydrogen atom is that although there is kinetic energy associated with  $\theta, \phi$  motion, the total energy is only dependent on the radial quantum number  $n$ :

$$\langle L_z^2/2mr^2 \rangle_{nl} = [l(l+1)\hbar^2/2m][\langle r^{-2} \rangle_{nl}] \quad (\text{IV.68})$$

$$\langle -(1/4\pi\epsilon_0)(e^2/r) \rangle_{nl} = -(e^2/4\pi\epsilon_0)\langle r^{-1} \rangle_{nl} \quad (\text{IV.69})$$

In order for the  $2s$  ( $l = 0$ ) and  $2p$  ( $l = 1$ ) orbitals to have the same energy,  $\langle r \rangle_{21} < \langle r \rangle_{20}$ . In general, as  $l$  increases for fixed  $n$ ,  $\langle r \rangle_{nl}$  decreases. The decreased Coulomb energy compensates for the increased angular kinetic energy.

Because  $S = 1/2$  for electrons, the total electron wavefunction is  $|\psi_{nlm}\rangle^{1/2}, m\rangle$  where the first part is the spatial function and the second part is the electron spin function. Each spatial function can be associated with either the  $m = 1/2$  or the  $m = -1/2$  spin function.

The orbitals for atoms with larger numbers of electrons are based on the hydrogen atom orbitals. Electrons are *fermions* which means that there can be only one electron per hydrogen atom wavefunction. For example, the ten electrons in neon are considered to occupy all of the  $n = 1$  and  $n = 2$  orbitals (5 spatial orbitals:  $1s, 2s, 2p$  ( $m = -1, 0, 1$ )).

The independence of energy on  $l$  for the hydrogen atom is not obtained for other atoms. The difference is interelectron repulsion.

Understanding electronic structure in molecules begins with creation of atomic orbitals whose spatial orientations are the same as those of the chemical bonds. These orbitals are linear combinations of the hydrogen atom orbitals. For example, the  $l = 1, m = \pm 1$  hydrogen orbitals have no preferred orientation in the  $xy$  plane but defined direction can be created by linear combinations of these orbitals. In particular:

$$\psi_{p_x} \propto (\psi_{1,+1} + \psi_{1,-1}) \propto \sin\theta(e^{i\phi} + e^{-i\phi})/2 = \sin\theta \cos\phi \quad (\text{IV.70})$$

$$\psi_{p_y} \propto (\psi_{1,+1} - \psi_{1,-1}) \propto \sin\theta(e^{i\phi} - e^{-i\phi})/2 = \sin\theta \sin\phi \quad (\text{IV.71})$$

Some molecular electronic spectra are interpreted in terms of perturbed atomic orbitals. For example, visible spectra of first-row transition metal complexes are often interpreted in terms of  $3d \leftarrow 3d$  transitions of the metal ion. Directional  $3d$  hydrogen atom orbitals are perturbed by the ligands of the complex. Note that these transitions violate the  $\Delta l = 1$  selection rule for hydrogen atom transitions.

Most molecular electronic spectra are understood as transitions between “molecular orbitals” which are linear combinations of atomic orbitals of different different atoms in the molecule. The individual atomic orbitals may be “hybridized” as linear combinations of the hydrogen atom orbitals which point along the chemical bond directions. A specific example is the tetrahedrally oriented  $2sp^3$  orbitals of carbon which are formed from linear combinations of the  $2s, 2p_x, 2p_y,$  and  $2p_z$  ( $l = 1, m = 0$ ) orbitals.

$$\frac{1}{2} 2s + (3/4)^{1/2} 2p_z \quad \text{points along } z \text{ direction} \quad (\text{IV.72})$$

$$\frac{1}{2} 2s - (1/12)^{1/2} 2p_z + (2/3)^{1/2} 2p_x \quad \text{lies in } xz \text{ plane} \quad (\text{IV.73})$$

$$\frac{1}{2} 2s - (1/12)^{1/2} 2p_z - (1/6)^{1/2} 2p_x + (1/2)^{1/2} 2p_y \quad (\text{IV.74})$$

$$\frac{1}{2} 2s - (1/12)^{1/2} 2p_z - (1/6)^{1/2} 2p_x - (1/2)^{1/2} 2p_y \quad (\text{IV.75})$$

Note that the four  $sp^3$  orbitals are orthonormal and that the total number of hybridized orbitals equals the number of input hydrogen atom orbitals.

The hydrogen molecule with hydrogen atoms  $A$  and  $B$  is the simplest example of molecular orbitals:

$$1s\sigma \propto 1s_A + 1s_B \quad (\text{IV.76})$$

$$1s\sigma^* \propto 1s_A - 1s_B \quad (\text{IV.77})$$

An electron in the  $1s\sigma$  “bonding” orbital has a higher probability of being between the two hydrogen nuclei than does an electron in the  $1s_A$  or the  $1s_B$  orbital. Electrons in this in-between region experience the attractive Coulomb interaction with both hydrogen nuclei and leads to lower overall energy relative to the atomic orbitals.

An electron in the  $1s\sigma^*$  “anti-bonding” orbital has lower probability of being between the two nuclei and has higher energy relative to the atomic orbitals.

Because they have opposite values of the spin quantum number  $m$ , the two electrons can both be in the  $1s\sigma$  orbital and form the chemical bond, i.e. a region of significant electron density between two nuclei.

A  $\pi$  molecular orbital is formed by a linear combination of  $p$  atomic orbitals whose direction is perpendicular to the internuclear axes.

Electronic spectral transitions are typically localized to molecular orbitals of a specific functional group within the molecule. In this context, the functional group is called a “chromophore”.