The Underpinnings of Chemistry:

(1) matter = nuclei + electrons
- electrons: $m_e, -e$
- nuclei: $m \approx Am_p, \quad q=Ze \; (A, Z \; \text{integers})$
  - nuclei and electrons are not changed in chemical processes

$$\frac{m_e}{m_p} = \frac{1}{1836}$$

(2) only forces are from Coulomb’s law:

$$V_{ij}(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|}$$

(3) motions / states governed by QM

$$\left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right\} \Psi(x, t) = i\hbar \frac{\partial \Psi}{\partial t}$$

wavefunction $\Psi(x,t)$

not

trajectory $\{x(t), p(t)\}$
Classical & QM H atoms:

classical H-atom: (macroscopic analogue)

QM H-atom:
- volume atom $\sim 10^{12}$ volume of $p^+$
- for macroscopic analogue, average $e^-$ radius $\sim 1$ km
- when thinking of molecular structure and intermolecular interactions best to think of nuclei as point particles and $e^-$ as diffuse charge distribution

Need an appreciation for $\Psi$ in order to understand electronic structure & interactions (& therefore molecular modeling)
Hydrogenic (1e) Atoms: (one of few exactly soluble cases)

\[ \hat{H} \psi = E \psi \]

time-independent Schrödinger equation, an eigenvalue equation

\[ \hat{H} = -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{4\pi\varepsilon_0} \frac{Z}{r} \]

“Hamiltonian” (energy) operator

- kinetic energy
- potential energy

\[ E \] total energy in state \( \psi \)

\[ \psi(x, y, z) = \psi(\vec{r}) \] wavefunction

\[ |\psi(\vec{r})|^2 \, dx\,dy\,dz \] probability of \( e \) being within \( dx\,dy\,dz \) of \( \vec{r} \)

\[ \rho(\vec{r}) = -e |\psi(\vec{r})|^2 \] electron density
Energy Spectrum:

\[ E = E(n) = -\frac{1}{2} \left( \frac{m_e e^4}{(4\pi\varepsilon_0)^2 \hbar^2} \right) \left( \frac{Z}{n} \right)^2 \]

\( n = 1, 2, 3, \ldots, \infty \)

useful to remember:

\[ E(n) / \text{eV} = -13.6 \left( \frac{Z}{n} \right)^2 \]

\[ E(n) / E_h = -\frac{1}{2} \left( \frac{Z}{n} \right)^2 \]

\( E_h = \text{“hartree”} \)

= atomic unit of energy

\[ \text{Atkins Fig. 13.8} \]

\[ \begin{array}{cccc}
1 & 1s & \text{“K” shell (n=1)} \\
[1] & & \\
2 & 2s & 2p & \text{“L” (n=2)} \\
3 & 3s & 3p & 3d & \text{“M” (n=3)} \\
\infty & & & \\
\end{array} \]
### Table 1.1 Useful quantities in atomic and other units

<table>
<thead>
<tr>
<th>Physical quantity (unit name)</th>
<th>Symbol</th>
<th>Value in a.u.</th>
<th>Value in SI units</th>
<th>Value(s) in other units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular momentum</td>
<td>$\hbar$</td>
<td>1</td>
<td>$1.055 \times 10^{-24}$ J s</td>
<td>$2.521 \times 10^{-25}$ cal s</td>
</tr>
<tr>
<td>Mass</td>
<td>$m_e$</td>
<td>1</td>
<td>$9.109 \times 10^{-31}$ kg</td>
<td>$1.519 \times 10^{-14}$ statC</td>
</tr>
<tr>
<td>Charge</td>
<td>$e$</td>
<td>1</td>
<td>$1.602 \times 10^{-19}$ C</td>
<td>$2.660 \times 10^{-21}$ C² J⁻¹ Å⁻¹</td>
</tr>
<tr>
<td>Vacuum permittivity</td>
<td>$4\pi\varepsilon_0$</td>
<td>1</td>
<td>$1.113 \times 10^{-10}$ C² J⁻¹ m⁻¹</td>
<td>$0.529$ Å</td>
</tr>
<tr>
<td>Length (bohr)</td>
<td>$a_0$</td>
<td>1</td>
<td>$5.292 \times 10^{-11}$ m</td>
<td>$52.9$ pm</td>
</tr>
<tr>
<td>Energy (hartree)</td>
<td>$E_h$</td>
<td>1</td>
<td>$4.360 \times 10^{-18}$ J</td>
<td>$627.51$ kcal mol⁻¹</td>
</tr>
<tr>
<td>Electric dipole moment</td>
<td>$\varepsilon_0 a_0^2 E_h^{-1}$</td>
<td>1</td>
<td>$8.478 \times 10^{-30}$ C m</td>
<td>$2.626 \times 10^3$ kJ mol⁻¹</td>
</tr>
<tr>
<td>Electric polarizability</td>
<td>$\varepsilon_0 a_0^2 E_h^{-1}$</td>
<td>1</td>
<td>$1.649 \times 10^{-41}$ C² m³ J⁻¹</td>
<td>$27.21$ eV</td>
</tr>
<tr>
<td>Planck’s constant</td>
<td>$\hbar$</td>
<td>2π</td>
<td>$6.626 \times 10^{-34}$ J s</td>
<td>$2.195 \times 10^9$ cm⁻¹</td>
</tr>
<tr>
<td>Speed of light</td>
<td>$c$</td>
<td>$1.370 \times 10^2$</td>
<td>$2.998 \times 10^8$ m s⁻¹</td>
<td>$2.542$ D</td>
</tr>
<tr>
<td>Bohr magneton</td>
<td>$\mu_B$</td>
<td>0.5</td>
<td>$9.274 \times 10^{-28}$ J T⁻¹</td>
<td></td>
</tr>
<tr>
<td>Nuclear magneton</td>
<td>$\mu_N$</td>
<td>2.723 $\times 10^{-4}$</td>
<td>$5.051 \times 10^{-27}$ J T⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

(from C. J. Cramer, "Computational Chemistry" (Wiley, NY, 2008)

### ENERGY CONVERSION FACTORS

$E = h \nu = h \bar{v} = kT; \ E_m = LE$

<table>
<thead>
<tr>
<th>Wavenumber $\bar{v}$</th>
<th>Frequency $\nu$</th>
<th>Energy $E$</th>
<th>Molar energy $E_m$</th>
<th>Temperature $T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm⁻¹</td>
<td>MHz</td>
<td>aJ</td>
<td>eV</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>1 cm⁻¹</td>
<td>1</td>
<td>2.997 925 × 10⁴</td>
<td>1.986 447 × 10⁻⁵</td>
<td>1.196 666 × 10⁻³</td>
</tr>
<tr>
<td>1 MHz</td>
<td>3.335 64 × 10⁻⁵</td>
<td>1</td>
<td>6.626 076 × 10⁻¹⁰</td>
<td>1.196 666 × 10⁻³</td>
</tr>
<tr>
<td>1 aJ</td>
<td>50.341 1</td>
<td>1</td>
<td>6.241 506</td>
<td>1.196 666 × 10⁻³</td>
</tr>
<tr>
<td>1 eV</td>
<td>806.5 54</td>
<td>0.160 217 7</td>
<td>3.674 931 × 10⁻²</td>
<td>1.196 666 × 10⁻³</td>
</tr>
<tr>
<td>1 $E_h$</td>
<td>219 474.63</td>
<td>4.359 748</td>
<td>27.214 7</td>
<td>1.196 666 × 10⁻³</td>
</tr>
<tr>
<td>1 kcal/mol</td>
<td>83.59 35</td>
<td>2.506 069 × 10⁶</td>
<td>1.660 540 × 10⁻³</td>
<td>1.196 666 × 10⁻³</td>
</tr>
<tr>
<td>1 kJ/mol</td>
<td>349 755</td>
<td>1.048 539 × 10⁷</td>
<td>6.947 700 × 10⁻³</td>
<td>1.196 666 × 10⁻³</td>
</tr>
<tr>
<td>1 K</td>
<td>0.695 039</td>
<td>2.083 67 × 10⁶</td>
<td>1.380 658 × 10⁻⁵</td>
<td>1.196 666 × 10⁻³</td>
</tr>
</tbody>
</table>

Examples of the use of this table: 1 aJ = 50.341 cm⁻¹

The symbol = should be read as meaning 'corresponds to' or 'is equivalent to'

(from "Quantities, Units, & Symbols in Physical Chemistry", J. Mills et al., 2nd Ed. (Blackwell, 1995).

1/13/2005

CHEM 408 - Sp05
Wavefunctions:

\[ \Psi_{n,l,m_l}(\vec{r}) = \Psi_{n,l,m_l}(r, \theta, \varphi) = R_{n,l}(r)Y_{l,m_l}(\theta, \varphi) \]

Quantum Numbers:

- \( n = 1, 2, 3, 4, \ldots \) principle; defines shell
- \( l = 0, 1, 2, 3, \ldots, (n-1) \) azimuthal; \((n,l)\) define subshell
- \( s, p, d, f, \ldots \)
- \( m_l = 0, \pm 1, \pm 2, \ldots, \pm l \) magnetic
Real Representations of $\Psi(r, \theta, \phi)$

$$1s = \frac{1}{\pi^{1/2}} \left( \frac{Z}{a} \right)^{3/2} e^{-Zr/a}$$
$$2s = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{3/2} \left( 2 - \frac{Zr}{a} \right) e^{-Zr/2a}$$
$$2p_z = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{5/2} e^{-Zr/2a} \cos \theta$$
$$2p_x = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{5/2} e^{-Zr/2a} \sin \theta \cos \phi$$
$$2p_y = \frac{1}{4(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{5/2} e^{-Zr/2a} \sin \theta \sin \phi$$
$$3s = \frac{1}{81(3\pi)^{1/2}} \left( \frac{Z}{a} \right)^{3/2} \left( 27 - 18 \frac{Zr}{a} + 2 \frac{Z^2r^2}{a^2} \right) e^{-Zr/3a}$$
$$3p_z = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{5/2} \left( 6 - \frac{Zr}{a} \right) e^{-Zr/3a} \cos \theta$$
$$3p_x = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{5/2} \left( 6 - \frac{Zr}{a} \right) e^{-Zr/3a} \sin \theta \cos \phi$$
$$3p_y = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{5/2} \left( 6 - \frac{Zr}{a} \right) e^{-Zr/3a} \sin \theta \sin \phi$$
$$3d_{z^2} = \frac{1}{81(6\pi)^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} (3 \cos^2 \theta - 1)$$
$$3d_{xz} = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin \theta \cos \theta \cos \phi$$
$$3d_{yz} = \frac{2^{1/2}}{81\pi^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin \theta \cos \theta \sin \phi$$
$$3d_{x^2-y^2} = \frac{1}{81(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin^2 \theta \cos 2\phi$$
$$3d_{xy} = \frac{1}{81(2\pi)^{1/2}} \left( \frac{Z}{a} \right)^{7/2} r^2 e^{-Zr/3a} \sin^2 \theta \sin 2\phi$$

$R(r)$ – The Radial Part of $\Psi(r, \theta, \varphi)$

Atkins, Fig. 13.5, 11
$Y(\theta, \varphi)$ – The Angular Part of $\Psi(r, \theta, \varphi)$

Atkins, Fig. 13.17, 18
Different Representations of Radial Behavior

\[ |\Psi(r)|^2 \, dv \]

Probability Density

\[ P(r)\, dr = 4\pi r^2 |\Psi(r)|^2 \, dr \]

Radial Distribution Fn.

Atkins, Fig. 13.14

Atkins, Fig. 13.15
H-atom Wavefunctions

$|\Psi(r)|^2 / a_0^3$

1s
2s
3s

$4\pi r^2 |\Psi(r)|^2 / a_0^2$

1s (×.5)
2s
3s

Penetration

Atkins, 13.16, 13.22

Radius, $r$

Radial distribution function, $P$

$Zr/a_0$
http://www.shef.ac.uk/chemistry/orbitron/

(6d orbitals)
Calculating Properties from $\Psi$

Observable properties are represented by operators $\hat{A}$ in QM:

1) if $\hat{A} \Psi = a \Psi$ where $a$ is a constant, then $A$ has the definite value $a$ in state $\Psi$

2) otherwise, the value of $A$ is not definite but the average (over many measurements) or “expectation value” is given by

$$< \hat{A} > = \int \Psi^* \hat{A} \Psi \, d\tau$$

$d\tau$ represents all coordinates, e.g. $dx dy dz$
\[ r_{n,l} = n^2 \left\{ 1 + \frac{1}{2} \left( 1 - \frac{l(l + 1)}{n^2} \right) \right\} \frac{a_0}{Z} \]