Atomic Orbitals

It is very customary to describe the wavefunctions of molecules using atomic orbitals as building blocks. The reason is that the electron density around atoms is really only slightly perturbed (on a percent basis) from the atoms. For H_2, the separated atoms have $2E_H = -27.2$ ev while $E_{H_2} = -31.85$ ev.

Therefore, before we move to molecules, the goal of this section is to become extremely familiar with atomic orbitals—not just those of H— but those of many-electron atoms as well.

One-Electron Atoms and Ions

1. Write the Schrodinger Equation

    system = $(+Z)$ and $(-)$, 2 point charges
          N   e

$$H = T_{e_{op}} + T_{N_{op}} - V_{Ne} = \frac{-\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{Ze^2}{r}$$

or, in atomic units:

$$H = \frac{-\nabla_e^2}{2} - \frac{\nabla_N^2}{2\left(\frac{m_N}{m_e}\right)} - \frac{Z}{r}$$

2. Transform to center-of-mass (internal) coordinate system. This makes the problem SOLVABLE exactly because it mimics a one-particle problem. You may think of it as keeping the nucleus fixed and looking only at the electron, but it's more general than that; you

see in the Schrodinger equation that $V = V(r)$; this defines a
CENTRAL FORCE PROBLEM. The solutions, in part, are useful for a
wide variety of spherical problems, such as seismic waves in the
earth, sound waves in a spherical cavity, tidal waves on a flooded
planet, to name only a few.* In fact, the three variables used can
be thought of as;

r = distance from center of earth

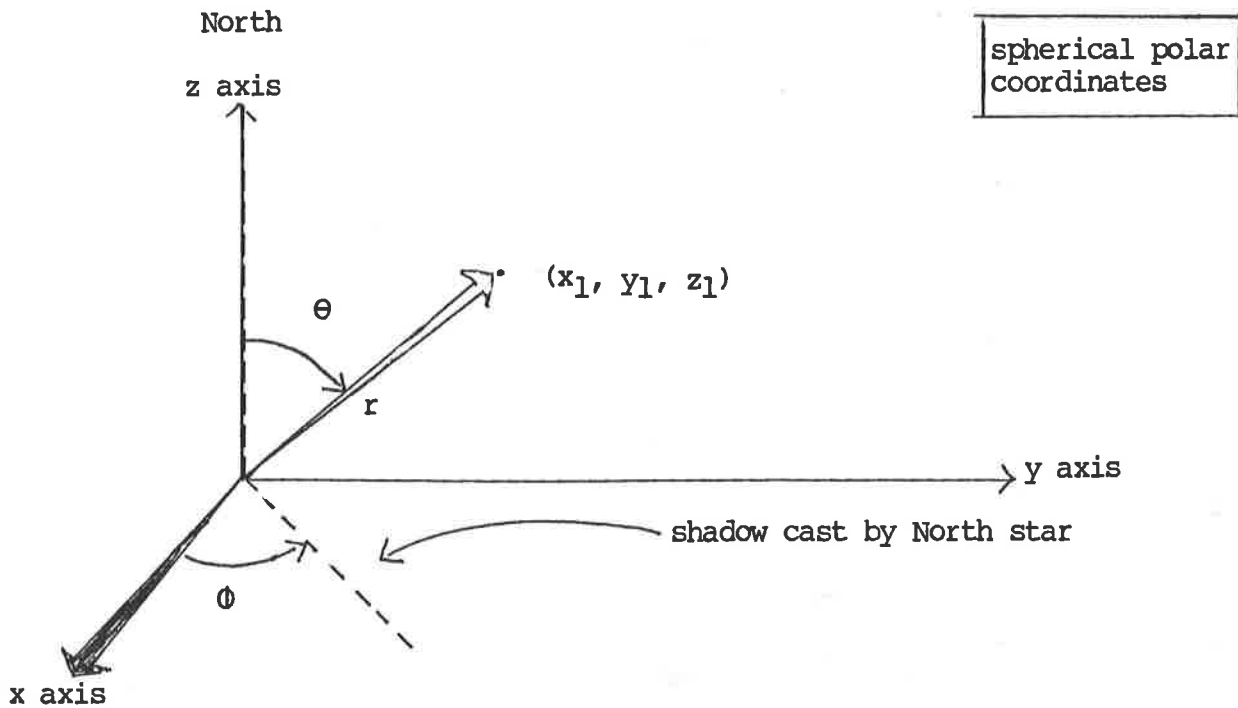θ = latitude ($0°$ = north pole = z axis, $90°$ = equator, $180°$ =
south pole)

ϕ = longitude ($0°$ = x axis)

$90°$ = y axis

$180°$ = −x axis

$270°$ = −y axis

$360°$ = back to x axis, etc.

North

z axis

| spherical polar |
| coordinates |

θ

(x_1, y_1, z_1)

r

y axis

shadow cast by North star

ϕ

x axis

*The math is equivalent to finding standing waves; it was worked out
long before Schrodinger's time. Thus, he didn't have to solve any new
equations.

The relation to x, y, and z (when center of earth is origin) is:

$$x_1 = r \sin \theta \cos \phi$$

$$y_1 = r \sin \theta \sin \phi$$

$$z_1 = r \cos \theta$$

$$dv = r^2 dr \sin \theta \, d\theta \, d\phi$$

Note that unlike x-, y-, z-space, we choose here to use volume increments whose sizes are not all equal; they depend on where you are. This has an effect on the slope and curvature operators since they have dx^2, dy^2 and dz^2 in them. Thus,

Curvature =

$$\nabla^2 = (\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}) + \frac{1}{r^2}(\frac{\partial^2}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta} \frac{\partial}{\partial \theta}) + \frac{1}{r^2\sin^2\theta} \frac{\partial^2}{\partial \phi^2}$$

$$\text{and } T_{op} = \frac{-\hbar^2}{2\mu} \nabla^2$$

$$\text{where } \mu = \text{reduced mass}, \quad \frac{m_N m_e}{m_N + m_e} \cong m_e$$

The Schrodinger equation then looks like:

$$H\Psi = E\Psi$$

$$(T_{op} + V_{op})\Psi = E\Psi$$

$$((T_{radial})_{op} + (T_{angular})_{op} + V)\Psi = E\Psi$$

$$[\frac{-\hbar^2}{2\mu}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) - \frac{\hbar^2}{2\mu r^2}(\frac{\partial^2}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial \theta}) - \frac{\hbar^2}{2\mu r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2} - \frac{z}{r}]\Psi = E\Psi$$

$$\left(T_{angular}\right)_{op} = \frac{L^2}{2\mu r^2}$$

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L^2 = total angular momentum squared operator

$$L^2 \psi = \ell(\ell + 1)\hbar^2 \psi$$

(you learned about ℓ in high school chemistry)

The form for ∇^2 here is different from, but is exactly <u>equivalent</u> to, that seen in most text books. (See <u>Levine, Chap. 6</u>.) The <u>important</u> thing is to note that the kinetic energy is divided into two basic types of motion:

    r- motion (radial) = head for the nucleus (China Syndrome)

    θ- and ϕ- motion (angular) = keep r constant, i.e., go in
               circular orbit (take the surface route)

Angular Momentum

<u>Very important</u>! The letter part of atomic orbital names (s, p, d, f...) tells you exactly the <u>total</u> square of angular momentum, L^2. For <u>all</u> central force problems:

$\ell = 0 \longrightarrow s$ $\ell = 3 \longrightarrow f$

$\ell = 1 \longrightarrow p$ $\ell = 23 \longrightarrow z$, etc.

$\ell = 2 \longrightarrow d$

Classically: $\dfrac{L^2}{2\mu r^2} = T_{angular}$

Quantum mechanics: $\dfrac{L^2}{2\mu r^2} = (T_{angular})_{op}$

$$L^2 = L_{op}^2$$

"Centrifugal Force"

Is this the fifth force of nature? Not at all! Nevertheless it is a useful concept since we (as masses in the classical mechanical description of the earth and its objects) have actually experienced "centrifugal force". The electron does too, it appears, because the r motion is affected by the θ and Φ motion, precisely in the common sense of centrifugal force.

Your old physics book says:

$$\text{Centrifugal force} = \frac{L^2}{2\mu r^3} = -\frac{d}{dr}\left(\frac{L^2}{2\mu r^2}\right)$$

so you see, $\frac{L^2}{2\mu r^2}$ which is $\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}$ behaves as the "centrifugal potential energy" but it is actually just the angular KINETC energy; therefore it's called a pseudo potential and its derivative, the centrifugal force, is a pseudo force.

However, pseudo or not, in a d orbital, where $\ell = 2$, the electron has a quite difficult time getting near the nucleus (remember how hard it is to get to the center of the merry-go-round?). The d electrons are easily pushed away from the nucleus, and this fact leads to the confusing nature of the transition metal part of the periodic table. Likewise and more so for f orbitals (Lanthanide series).