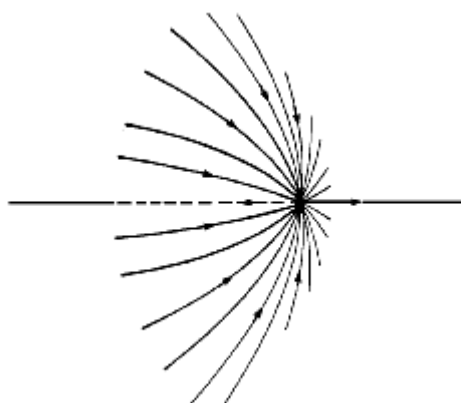


Modelling Techniques for Organic Molecules

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The Topological Atom

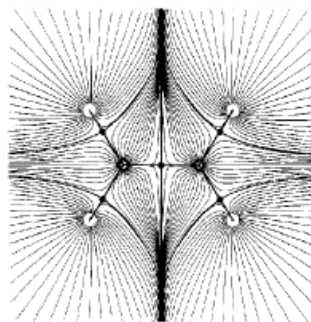
Quantum mechanically, an atom is represented as a region in real space bounded by surfaces through which there is no flux in the gradient field of the charge density. The nucleus of each atom is the point attractor of the gradient field, just as the proton is the point attractor of the electric field. Similarly, interatomic surfaces form in regions where this “zero-flux” boundary condition is satisfied. In simpler terms, the electron density function is bounded by a surface formed where $\nabla\rho(\vec{r})$ is tangent to that surface.



Theorem

A surface $S(\vec{r})$ is defined where $\nabla\rho(\vec{r}) \cdot \hat{n}(\vec{r}) = 0$ everywhere on $S(\vec{r})$

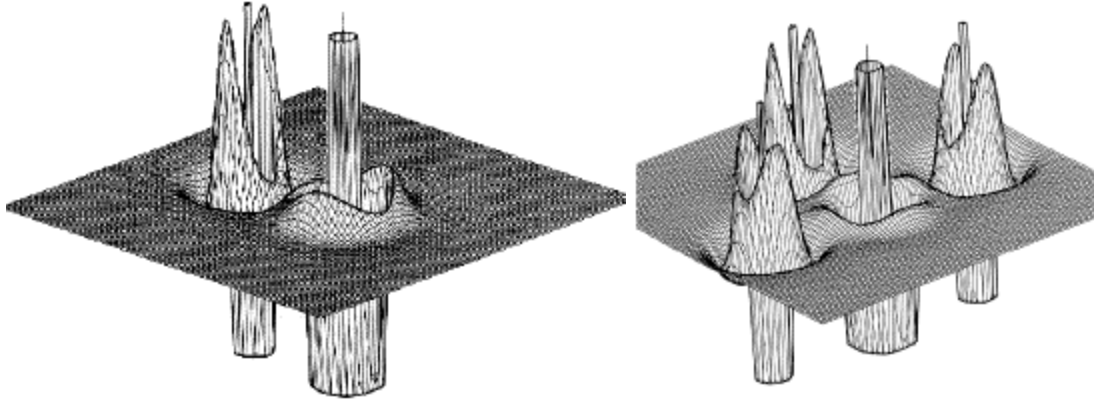
There are regions throughout space where the electron density $\rho(\vec{r})$ experiences a critical point, where $\nabla\rho(\vec{r}) = 0$. This point defines the interatomic surface; the point where the electron densities from neighboring atoms meet and terminate. There is a single point where the normal vectors of each atom lie parallel to each other. The line along which $\nabla\rho(\vec{r}) = 0$ (indicating the path of maximum density) and is parallel to these vectors defines the orientation of the molecule, and the direction of bonding.



C₂H₄

Since the nuclei of the constituent atoms in a molecule are point attractors for the density-gradient field, a displacement of the positioning of the nuclei will result in an abrupt change in the density distribution. Certain configurations will result in singular points in the gradient, indicating regions where bonds are broken and the molecular structure is altered.

The Laplacian of the electron density $\nabla^2 \rho(\vec{r})$ goes further in describing the charge distribution around an atom. For a free atom, the valence shell will have a uniform spherical distribution corresponding to $\nabla^2 \rho(\vec{r}) = 0$. However, in the presence of additional particle interactions, the distribution changes to yield regions of a large concentration of charge ($\nabla^2 \rho(\vec{r}) > 0$) and regions with depletion in charge ($\nabla^2 \rho(\vec{r}) < 0$). The number and location of the local maxima of $\nabla^2 \rho(\vec{r})$ in the valence shell give the position and number of electron pairs present in the outer valence shell of the atom. A chemical reaction is thus represented by the filling of a region of depleted charge (behaving as electrophiles) with charge from a highly concentrated region (behaving as nucleophiles).



ClF₃

The Hydrogen Atom

The Schrödinger Equation for a single electron Hydrogen atom is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)+V_c(\vec{r})\psi(\vec{r},t)=i\hbar\frac{\partial}{\partial t}[\psi(\vec{r},t)]$$

Where $V_c(\vec{r})$ is the Coulomb potential existing from electron-proton interactions.

Namely,

$$V_c(\vec{r})=-\frac{e^2}{r}$$

Separating the Hydrogen wave function into spatial and temporal components

$\psi(\vec{r},t)=\phi_s(\vec{r})T(t)$ allows for the solution of the Time-Independent Schrödinger

Equation

$$-\frac{\hbar^2}{2m}\nabla^2\phi(\vec{r})-\frac{e^2}{r}\phi(\vec{r})=E\phi(\vec{r})$$

The solution to the spatial wave function yields quantized angular momentum and energy states corresponding to the quantum numbers n , ℓ and m . The spatial solution consists of an angular component $Y_{lm}(\theta,\varphi)$ and a radial component $R_{nl}(r)$ such that

$$\phi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi)$$

The solutions for $R_{nl}(r)$ satisfy the differential equation

$$\frac{d^2}{d\rho^2}(\rho R(r))+2R(r)-\frac{\ell(\ell+1)}{\rho}R(r)=n\rho R(r)$$

The solutions for the first 3 states are given below.

$$\begin{array}{lll}
n = 1 & l = 0 & R_{10}(r) = \frac{2}{\sqrt{a^3}} e^{-\frac{r}{a}} \\
n = 2 & l = 0 & R_{20}(r) = \frac{1}{\sqrt{2a^3}} \left(1 - \frac{r}{2a}\right) e^{-\frac{r}{2a}} \\
& l = 1 & R_{21}(r) = \frac{1}{2\sqrt{6a^3}} \frac{r}{a} e^{-\frac{r}{2a}} \\
n = 3 & l = 0 & R_{30}(r) = \frac{2}{3\sqrt{3a^3}} \left[1 - \frac{2}{3}\left(\frac{r}{a}\right) + \frac{2}{27}\left(\frac{r}{a}\right)^2\right] e^{-\frac{r}{3a}} \\
& l = 1 & R_{31}(r) = \frac{1}{27\sqrt{6a^3}} \frac{r}{a} \left(1 - \frac{r}{6a}\right) e^{-\frac{r}{3a}} \\
& l = 2 & R_{32}(r) = \frac{4}{81\sqrt{30a^3}} \left(\frac{r}{a}\right)^2 e^{-\frac{r}{3a}}
\end{array}$$

Now , using the results for the generated radial functions, and the identity

$$\langle r^k \rangle = \int_0^\infty R(r)^* r^k R(r) r^2 dr = \int_0^\infty R(r)^2 r^{k+2} dr$$

and

$$r = a_0 n^2$$

Then

$$\langle r^k \rangle = \frac{a_0^{k+1}}{2} \int_{\text{all states}} R(a_0 n^2)^2 n^{k+1} dn$$

Yielding

$$\begin{aligned}
\left\langle \frac{1}{r} \right\rangle &= \frac{1}{a_0 n^2} \\
\left\langle \frac{1}{r^2} \right\rangle &= \frac{1}{a_0^2 \left[n^3 \left(\ell + \frac{1}{2} \right) \right]} \\
\left\langle \frac{1}{r^3} \right\rangle &= \frac{1}{a_0^3 \left[n^3 \ell \left(\ell + \frac{1}{2} \right) (\ell + 1) \right]}
\end{aligned}$$

Thus, the average electric field of the Hydrogen atom is given by

$$\langle \vec{E} \rangle = -e \left\langle \frac{1}{r^2} \right\rangle \hat{r} = -\frac{e}{a_o^2 \left[n^3 \left(\ell + \frac{1}{2} \right) \right]} \hat{r}$$

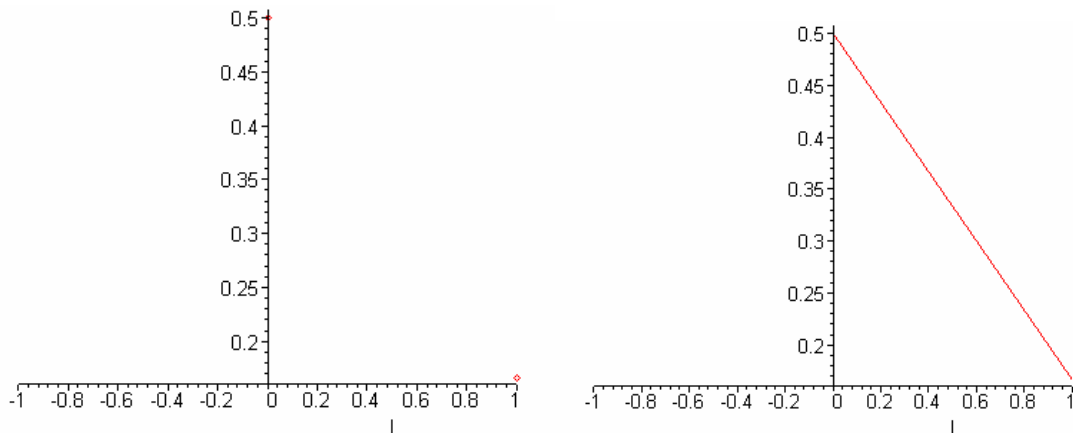
And the average potential is expressed as

$$\langle V \rangle = -e^2 \left\langle \frac{1}{r} \right\rangle = -\frac{e^2}{a_o n^2}$$

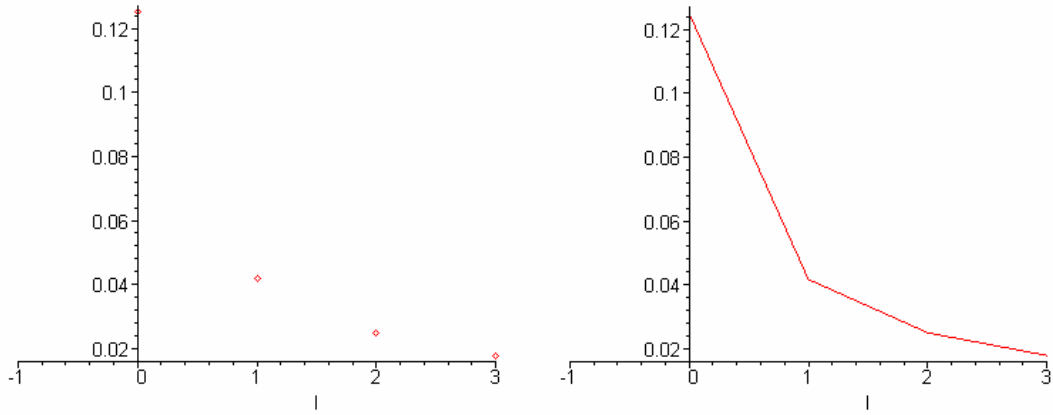
Theorem

The electric field experienced by the electron from the proton is affected by the rotational state (governed by ℓ), since the charge distribution changes for each state. However, the potential depends only on the energy level (orbital) the electron occupies. For any given energy level n , there are n possible electric fields, one for each value of $\ell = 0..n-1$.

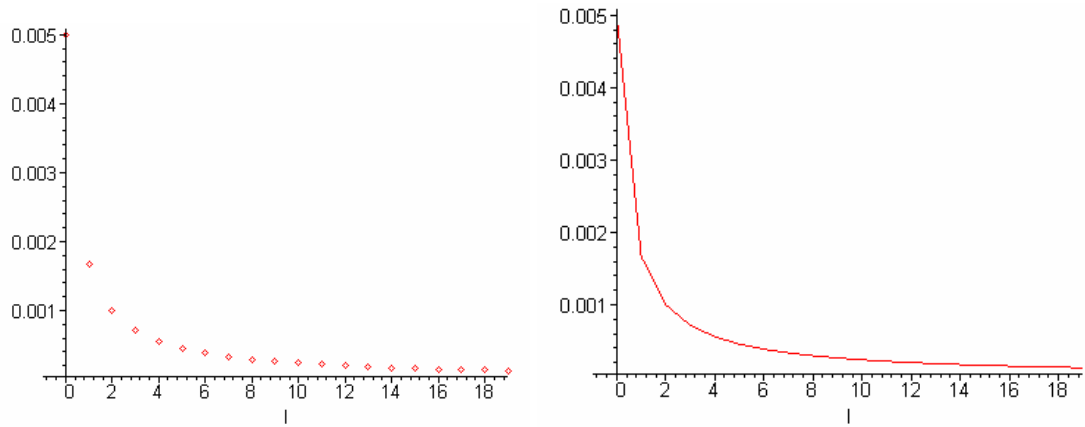
Electric Field Strength for n=2 State



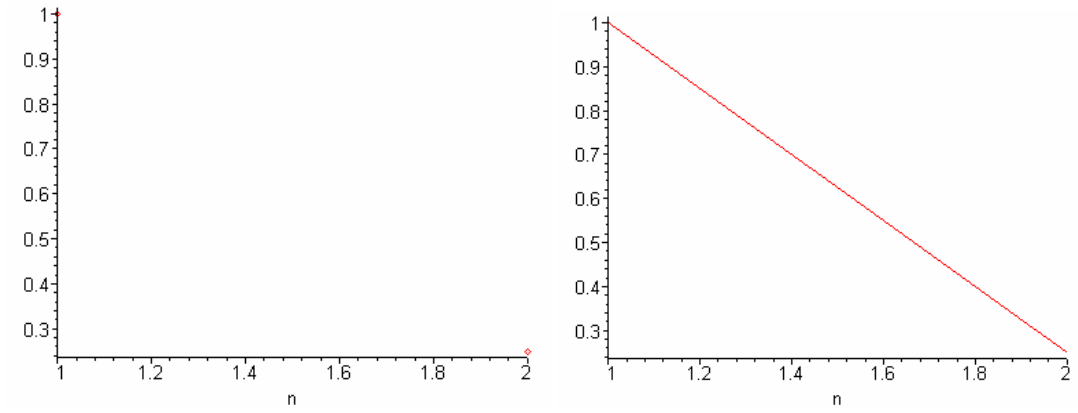
Electric Field Strength for n=4 State



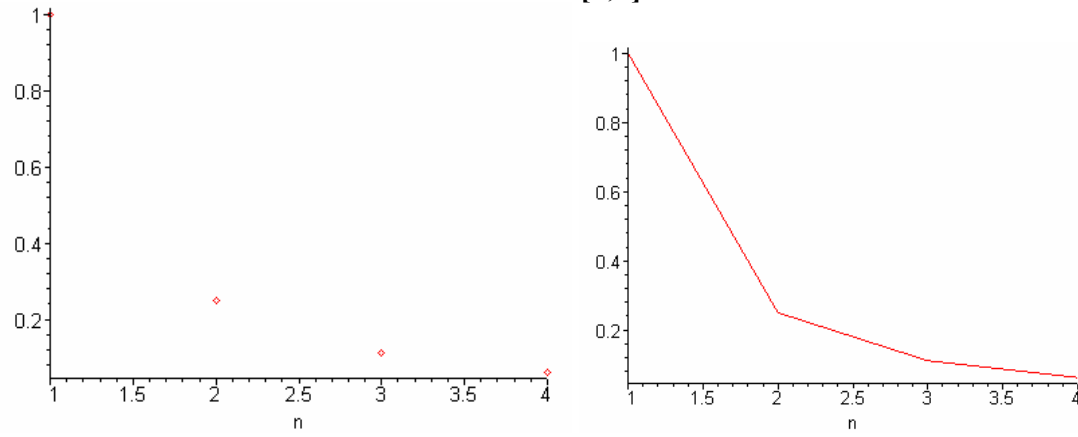
Electric Field Strength for n=20 State



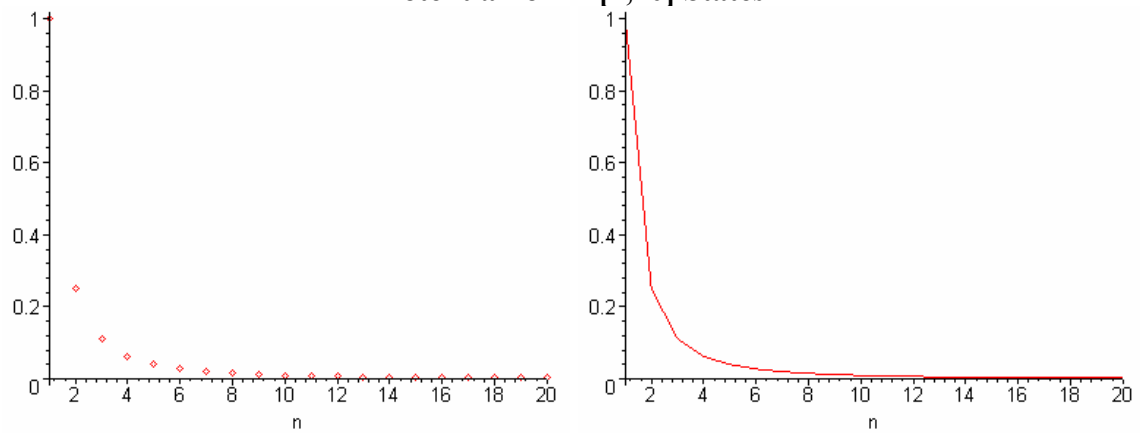
Potential for $n=[1,2]$ States



Potential for $n=[1,4]$ States



Potential for $n=[1,20]$ States



In the limit that $n \rightarrow \infty$, i.e. the electron is far removed from the nucleus, the potential and electric field experienced by the electron approach the classical values:

$$\lim_{n \rightarrow \infty} \langle V \rangle = -\frac{e^2}{r}, \lim_{n \rightarrow \infty} \langle \vec{E} \rangle = -\frac{e^2}{r^2} \hat{r}; r \gg a_0$$

There are, of course, additional potentials due to the spin-orbit interaction V_{SL} , spin-spin interaction V_{SS} , and magnetic moment interaction V_M . These are given by

$$V_{SL} = \frac{e^2}{2m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

$$V_{SS} = -\frac{1}{c^2} \left[\frac{2}{3} g_S g_I \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S} \cdot \vec{I} \nabla^2 \left(\frac{1}{r} \right) \right]$$

$$V_M = \frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) \cdot \vec{B}$$

Thus, the proper Time Independent Schrödinger Equation including all possible interactions is

$$-\frac{\hbar^2}{2m} \nabla^2 \phi(\vec{r}) + \left(\frac{e^2}{2m^2 c^2 r^3} \vec{S} \cdot \vec{L} - \frac{1}{c^2} \left[\frac{2}{3} g_S g_I \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S} \cdot \vec{I} \nabla^2 \left(\frac{1}{r} \right) \right] + \frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) \cdot \vec{B} - \frac{e^2}{r} \right) \phi(\vec{r}) = E \phi(\vec{r})$$

The spin states \vec{S} are given by the Pauli matrices:

$$S_x |\kappa\rangle = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} |\kappa\rangle$$

$$S_y |\kappa\rangle = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} |\kappa\rangle$$

$$S_z |\kappa\rangle = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} |\kappa\rangle$$

$$\text{Where } |k\rangle = \begin{cases} \begin{pmatrix} 1 \\ 0 \end{pmatrix}; |k\rangle = \left| +\frac{1}{2} \right\rangle \\ \begin{pmatrix} 0 \\ 1 \end{pmatrix}; |k\rangle = \left| -\frac{1}{2} \right\rangle \end{cases}$$

The angular momentum states \vec{L} are denoted in matrix form by

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} \langle l1| & \langle l0| & \langle l-1| \\ 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

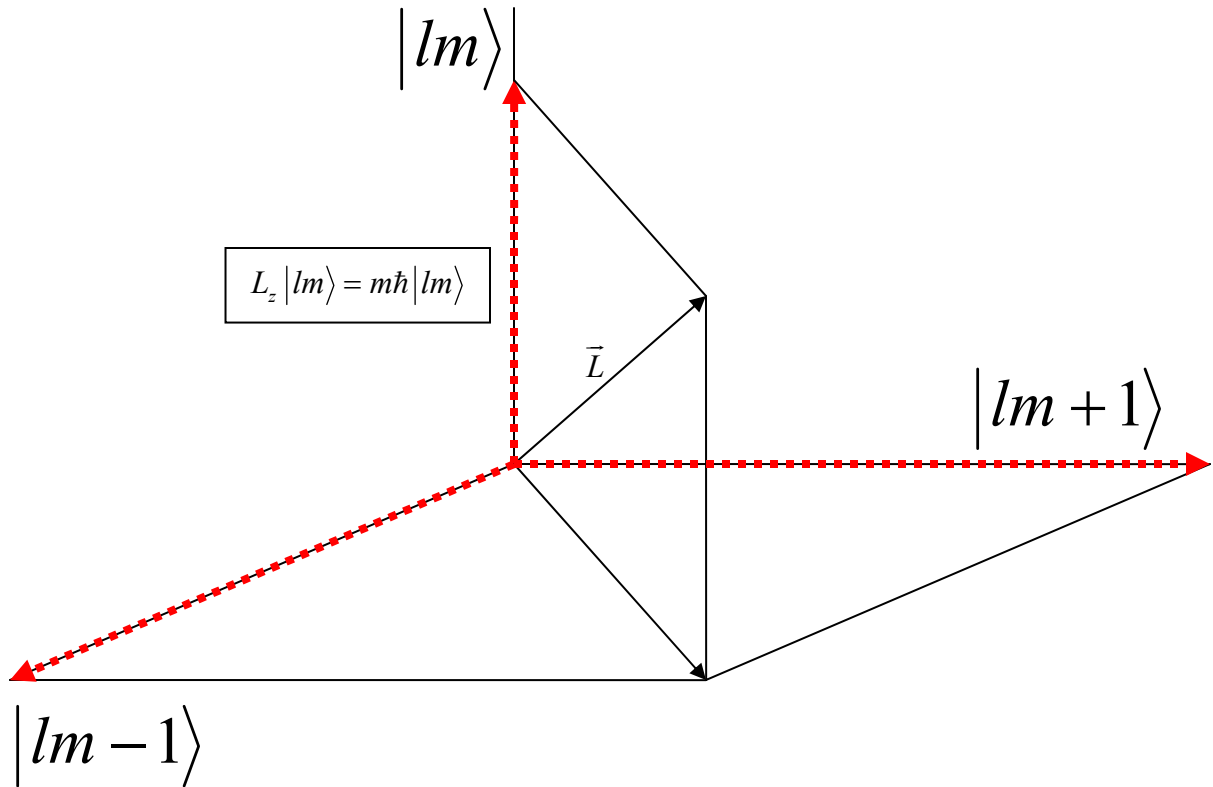
$$L_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} \langle l1| & \langle l0| & \langle l-1| \\ 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$L_z = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} \langle l1| & \langle l0| & \langle l-1| \\ 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Where $|l1\rangle, |l0\rangle, |l-1\rangle$ are the basis vectors for the momentum space of the electron, and are determined by the raising and lowering operator identities:

$$L_+ |lm\rangle = \hbar \sqrt{l(l+1) - m(m+1)} |l, m+1\rangle$$

$$L_- |lm\rangle = \hbar \sqrt{l(l+1) - m(m-1)} |l, m-1\rangle$$



Transitions between States

For stationary states, the wave function can be written as

$$\psi(\vec{r}, t) = \psi_{n\ell m}(\vec{r}) e^{-\frac{iE_n t}{\hbar}}$$

In this case the probability density is independent of time:

$$|\psi(\vec{r}, t)|^2 = \psi(\vec{r}, t)^* \psi(\vec{r}, t) = [\psi_{n\ell m}(\vec{r})]^2$$

For changing transition states, the initial and final states must be considered:

$$\text{(Initial State)} \quad \psi_1(\vec{r}, t) = \psi_{n\ell m}(\vec{r}) e^{-\frac{iE_n t}{\hbar}}$$

$$\text{(Final State)} \quad \psi_2(\vec{r}, t) = \psi_{n'\ell'm'}(\vec{r}) e^{-\frac{iE_{n'} t}{\hbar}}$$

To find transitions between the 2 states, a new wave function is needed which is a linear combination of the 2:

$$\psi(\vec{r}, t) = C_1 \psi_{n\ell m}(\vec{r}) e^{-\frac{iE_n t}{\hbar}} + C_2 \psi_{n'\ell'm'}(\vec{r}) e^{-\frac{iE_{n'} t}{\hbar}}$$

Note that this creates a certain probability of the electron occupying both states:

$$\begin{aligned}
 P(\vec{r}, t) &= \int_{\text{all space}} \left[C_1 \psi_{n\ell m}(\vec{r}) e^{\frac{iE_n t}{\hbar}} + C_2 \psi_{n'\ell' m'}(\vec{r}) e^{\frac{iE_{n'} t}{\hbar}} \right]^* \left[C_1 \psi_{n\ell m}(\vec{r}) e^{\frac{iE_n t}{\hbar}} + C_2 \psi_{n'\ell' m'}(\vec{r}) e^{\frac{iE_{n'} t}{\hbar}} \right] dV \\
 &= \int_{\text{all space}} \left[C_1^* \psi_{n\ell m}^*(\vec{r}) e^{\frac{iE_n t}{\hbar}} + C_2^* \psi_{n'\ell' m'}^*(\vec{r}) e^{\frac{iE_{n'} t}{\hbar}} \right] \left[C_1 \psi_{n\ell m}(\vec{r}) e^{\frac{iE_n t}{\hbar}} + C_2 \psi_{n'\ell' m'}(\vec{r}) e^{\frac{iE_{n'} t}{\hbar}} \right] dV \\
 &= C_1^* C_1 \int_{\text{all space}} \psi_{n\ell m}^* \psi_{n\ell m} dV + C_2^* C_2 \int_{\text{all space}} \psi_{n'\ell' m'}^* \psi_{n'\ell' m'} dV \\
 &\quad + C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^* \psi_{n'\ell' m'} e^{\frac{i(E_n - E_{n'}) t}{\hbar}} dV + C_2^* C_1 \int_{\text{all space}} \psi_{n'\ell' m'}^* \psi_{n\ell m} e^{\frac{i(E_{n'} - E_n) t}{\hbar}} dV \\
 &= |C_1|^2 + |C_2|^2 + C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^* \psi_{n'\ell' m'} e^{\frac{i(E_n - E_{n'}) t}{\hbar}} dV + C_2^* C_1 \int_{\text{all space}} \psi_{n'\ell' m'}^* \psi_{n\ell m} e^{\frac{i(E_{n'} - E_n) t}{\hbar}} dV
 \end{aligned}$$

Using $\left. \begin{matrix} A = a + bi \\ B = a - bi \end{matrix} \right\} A + B = 2a$, then

$$P(\vec{r}, t) = |C_1|^2 + |C_2|^2 + 2 \operatorname{Re} \left[C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^* \psi_{n'\ell' m'} e^{\frac{i(E_n - E_{n'}) t}{\hbar}} dV \right]$$

Using Euler's theorem

$$e^{i\left(\frac{E_n - E_{n'}}{\hbar} t\right)} = \cos\left(\frac{E_n - E_{n'}}{\hbar} t\right) + i \sin\left(\frac{E_n - E_{n'}}{\hbar} t\right)$$

Then

$$P(\vec{r}, t) = |C_1|^2 + |C_2|^2 + 2 \cos\left(\frac{E_n - E_{n'}}{\hbar} t\right) \operatorname{Re} \left[C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^* \psi_{n'\ell' m'} dV \right]$$

Now, the average position $\langle \vec{r} \rangle$ of the electron from the potential source (i.e. nucleus) can be found

$$\langle \vec{r} \rangle = \int_{\text{all space}} \left[C_1 \psi_{n\ell m}(\vec{r}) e^{\frac{iE_n t}{\hbar}} + C_2 \psi_{n'\ell' m'}(\vec{r}) e^{\frac{iE_{n'} t}{\hbar}} \right]^* \left[C_1 \psi_{n\ell m}(\vec{r}) e^{\frac{iE_n t}{\hbar}} + C_2 \psi_{n'\ell' m'}(\vec{r}) e^{\frac{iE_{n'} t}{\hbar}} \right] dV$$

$$\langle \vec{r} \rangle = \int_{\text{all space}} \left[C_1^* \psi_{n\ell m}^*(\vec{r}) e^{\frac{iE_n t}{\hbar}} + C_2^* \psi_{n'\ell' m'}^*(\vec{r}) e^{\frac{iE_{n'} t}{\hbar}} \right] \left[C_1 \psi_{n\ell m}(\vec{r}) e^{\frac{iE_n t}{\hbar}} + C_2 \psi_{n'\ell' m'}(\vec{r}) e^{\frac{iE_{n'} t}{\hbar}} \right] dV$$

$$\begin{aligned} \langle \vec{r} \rangle &= |C_1|^2 \int_{\text{all space}} \psi_{n\ell m}^*(\vec{r}) \psi_{n\ell m} dV + |C_2|^2 \int_{\text{all space}} \psi_{n'\ell' m'}^*(\vec{r}) \psi_{n'\ell' m'} dV \\ &+ C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^*(\vec{r}) \psi_{n'\ell' m'} e^{\frac{i(E_n - E_{n'}) t}{\hbar}} dV + C_2^* C_1 \int_{\text{all space}} \psi_{n'\ell' m'}^*(\vec{r}) \psi_{n\ell m} e^{\frac{i(E_{n'} - E_n) t}{\hbar}} dV \end{aligned}$$

$$\langle \vec{r} \rangle = C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^*(\vec{r}) \psi_{n'\ell' m'} e^{\frac{i(E_n - E_{n'}) t}{\hbar}} dV + C_2^* C_1 \int_{\text{all space}} \psi_{n'\ell' m'}^*(\vec{r}) \psi_{n\ell m} e^{\frac{i(E_{n'} - E_n) t}{\hbar}} dV$$

$$\langle \vec{r} \rangle = C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^*(\vec{r}) \psi_{n'\ell' m'} e^{\frac{i(E_n - E_{n'}) t}{\hbar}} dV + \left[C_2^* C_1 \int_{\text{all space}} \psi_{n'\ell' m'}^*(\vec{r}) \psi_{n\ell m} e^{\frac{i(E_{n'} - E_n) t}{\hbar}} dV \right]^*$$

Using $\left. \begin{matrix} A = a + bi \\ B = a - bi \end{matrix} \right\} A + B = 2a$, then

$$\langle \vec{r} \rangle = 2 \operatorname{Re} \left[C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^*(\vec{r}) \psi_{n'\ell'm'} e^{i \frac{E_n - E_{n'}}{\hbar} t} dV \right]$$

Using Euler's theorem

$$e^{i \left(\frac{E_n - E_{n'}}{\hbar} t \right)} = \cos \left(\frac{E_n - E_{n'}}{\hbar} t \right) + i \sin \left(\frac{E_n - E_{n'}}{\hbar} t \right)$$

Then

$$\langle \vec{r} \rangle = 2 \cos \left(\frac{E_n - E_{n'}}{\hbar} t \right) \operatorname{Re} \left[C_1^* C_2 \int_{\text{all space}} \psi_{n\ell m}^*(\vec{r}) \psi_{n'\ell'm'} dV \right]$$

Thus, the expected position of the electron oscillates with a frequency determined by the energy differences between the initial and final states.

The 2 Electron Atom

Consider an atom consisting of 2 electrons and 2 protons in the nucleus. The Hamiltonian of the atom is given as

$$H = -\frac{\hbar^2}{2\mu} (\nabla_1^2 + \nabla_2^2) + V(\vec{r}_1, \vec{r}_2)$$

This time, the potentials felt by both electrons from the nucleus must be considered, as well as those due to inter-particle repulsive forces between them. A potential describing these interactions can be given by

$$V = \sum_{i=1}^2 \left(-\frac{Z_i e^2}{r_i} \right) + \sum_{i=1}^2 \sum_{j \neq i}^2 \left(\frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right)$$

Notice the Z_i in the expression for the potential. It would have been trivial to force Ze to be the nuclear charge felt by all electrons, but that would neglect the fact that outer electrons would be less attracted, due to repulsions from inner electrons. So, instead, the *effective nuclear charge* $Z_i e$ "felt" by each electron must be considered.

Thus, for the inner most electron, it will feel the full nuclear attraction. For the outer electron, it will sense a nuclear charge of

$$Ze - (Z-1)e = e$$

So, the Hamiltonian for the 2 electron atom appears as

$$H = -\frac{\hbar^2}{2\mu}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{e^2}{r_2} + \sum_{i=1}^2 \sum_{j \neq i}^2 \left(\frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right)$$

Consider the wave function representing a 2 particle system under the influence of a central potential. Solutions of the form $\psi(\vec{r}_1, \vec{r}_2, t) = \psi_1(\vec{r}_1, t)\psi_2(\vec{r}_2, t)$ are desired. Using this in the Hamiltonian above,

$$H\psi(\vec{r}_1, \vec{r}_2, t) = -\frac{\hbar^2}{2\mu}(\psi_2(\vec{r}_2, t)\nabla_1^2\psi_1(\vec{r}_1, t) + \psi_1(\vec{r}_1, t)\nabla_2^2\psi_2(\vec{r}_2, t)) + V(\vec{r}_1, \vec{r}_2)\psi_1(\vec{r}_1, t)\psi_2(\vec{r}_2, t)$$

Or

$$H\psi(\vec{r}_1, \vec{r}_2, t) = -\psi_2(\vec{r}_2, t) \left[\frac{\hbar^2}{2\mu} \nabla_1^2 \psi_1(\vec{r}_1, t) \right] - \psi_1(\vec{r}_1, t) \left[\frac{\hbar^2}{2\mu} \nabla_2^2 \psi_2(\vec{r}_2, t) \right] + V(\vec{r}_1, \vec{r}_2)\psi_1(\vec{r}_1, t)\psi_2(\vec{r}_2, t)$$

First, consider the spatial component $\psi(\vec{r}_1, \vec{r}_2, t) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)T(t)$. For the time-independent Schrödinger Equation, the eigenvalue problem is given by

$$\frac{1}{\phi_1(\vec{r}_1)} \left[\frac{\hbar^2}{2\mu} \nabla_1^2 \phi_1(\vec{r}_1) \right] - \frac{1}{\phi_2(\vec{r}_2)} \left[\frac{\hbar^2}{2\mu} \nabla_2^2 \phi_2(\vec{r}_2) \right] + V(\vec{r}_1, \vec{r}_2) = E$$

At first, it may appear that the only means of solving this is numerically. However, an acceptable form of the potential is already known, namely

$$V(\vec{r}_1, \vec{r}_2) = \frac{2e^2}{r_1} - \frac{e^2}{r_2} + \sum_{i=1}^2 \sum_{j \neq i}^2 \left(\frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right).$$

Also, if the energy is to be of the form $E = E_1 + E_2$, this yields

$$\left\{ -\frac{1}{\phi_1(\vec{r}_1)} \left[\frac{\hbar^2}{2\mu} \nabla_1^2 \phi_1(\vec{r}_1) \right] - \frac{2e^2}{r_1} \right\} + \left\{ -\frac{1}{\phi_2(\vec{r}_2)} \left[\frac{\hbar^2}{2\mu} \nabla_2^2 \phi_2(\vec{r}_2) \right] - \frac{e^2}{r_2} \right\} + \sum_{i=1}^2 \sum_{j \neq i}^2 \left(\frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right) = \{E_1\} + \{E_2\}$$

This is becoming more interesting, since if it is possible to express the potential in the form $\frac{e^2}{|\vec{r}_2 - \vec{r}_1|} = V_1(\vec{r}_1) + V_2(\vec{r}_2)$, it reduces the problem to solving 2 separate Hydrogenic equations, for which the solutions are known.

$$\left\{ -\frac{1}{\varphi_1(\vec{r}_1)} \left[\frac{\hbar^2}{2\mu} \nabla_1^2 \varphi_1(\vec{r}_1) \right] - \frac{2e^2}{r_1} + V_1(\vec{r}_1) \right\} + \left\{ -\frac{1}{\varphi_2(\vec{r}_2)} \left[\frac{\hbar^2}{2\mu} \nabla_2^2 \varphi_2(\vec{r}_2) \right] - \frac{e^2}{r_2} + V_2(\vec{r}_2) \right\} = \{E_1\} + \{E_2\}$$

This yields two separate equations:

$$-\frac{1}{\varphi_1(\vec{r}_1)} \left[\frac{\hbar^2}{2\mu} \nabla_1^2 \varphi_1(\vec{r}_1) \right] - \frac{2e^2}{r_1} + V_1(\vec{r}_1) = E_1$$

$$-\frac{1}{\varphi_2(\vec{r}_2)} \left[\frac{\hbar^2}{2\mu} \nabla_2^2 \varphi_2(\vec{r}_2) \right] - \frac{e^2}{r_2} + V_2(\vec{r}_2) = E_2$$

An estimation of the values for $V_1(\vec{r}_1)$ and $V_2(\vec{r}_2)$ can be done by evaluating the full potential of each electron at certain limits.

For the first electron, at close distances it must feel the full potential,

so $\lim_{r_1 \rightarrow 0} V_1(\vec{r}_1) = -\frac{Ze^2}{r_1}$. At larger distances, the electron will be shielded so it will feel a

potential of $-\frac{e^2}{r_1}$, so $\lim_{r_1 \rightarrow \infty} V_1(\vec{r}_1) = -\frac{e^2}{r_1}$. Thus, a reasonable approximation is

$$V_1(\vec{r}_1) = -Z_{eff}(\vec{r}_1) \frac{e^2}{r_1}$$

Where $Z_{eff}(\vec{r})$ is the effective nuclear charge experienced by the electron at position \vec{r} .

Similarly for the second electron,

$$V_2(\vec{r}_2) = -Z_{eff}(\vec{r}_2) \frac{e^2}{r_2}$$

It is now a more arbitrary task to solve the two separate Hydrogenic equations:

$$-\frac{1}{\varphi_1(\vec{r}_1)} \left[\frac{\hbar^2}{2\mu} \nabla_1^2 \varphi_1(\vec{r}_1) \right] - Z_{\text{eff}}(\vec{r}_1) \frac{e^2}{r_1} = E_1$$

$$-\frac{1}{\varphi_2(\vec{r}_2)} \left[\frac{\hbar^2}{2\mu} \nabla_2^2 \varphi_2(\vec{r}_2) \right] - Z_{\text{eff}}(\vec{r}_2) \frac{e^2}{r_2} = E_2$$

The effective nuclear charge decreases exponentially outward from the nucleus, and is approximated by

$$Z_{\text{eff}}(\vec{r}) = Z \left(e^{-\frac{r}{Za_0}} \right)$$

The spin-orbit interaction for an electron in a complex system can be expressed in a similar fashion to the single-electron atom:

$$V_{SL_i} = \frac{\vec{S}_i \cdot \vec{L}_i}{2m^2 c^2} \left[\frac{1}{r_i} \frac{d}{dr} (V_c(\vec{r}_i)) \right]$$

$$V_{SS_i} = -\frac{1}{c^2} \left[\frac{2}{3} g_S g_I \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S}_i \cdot \vec{\nabla}^2 \left(\frac{1}{r_i} \right) \right]$$

$$V_{M_i} = \frac{\mu_B}{\hbar} (\vec{L}_i + 2\vec{S}_i) \cdot \vec{B}$$

Where $V_c(\vec{r}) = -\frac{Ze^2}{r}$ and thus $\frac{1}{r} \frac{d}{dr} [V_c(\vec{r})] = \frac{Ze^2}{r^3}$.

Hence, the potential approximation (including spin-angular momentum interaction) for each electron in a complex system is

$$V_i(\vec{r}_i) = -\frac{Ze^2}{r_i} \left(e^{-\frac{r_i}{Za_0}} \right) + \frac{Ze^2 \vec{S}_i \cdot \vec{L}_i}{2m_i^2 c^2 r_i^3} - \frac{1}{c^2} \left[\frac{2}{3} g_S g_I \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S}_i \cdot \vec{\nabla}^2 \left(\frac{1}{r_i} \right) \right] + \frac{\mu_B}{\hbar} (\vec{L}_i + 2\vec{S}_i) \cdot \vec{B}$$

Finally, the time independent Schrödinger Equation for each particle of a 2 electron atom appears as

$$-\frac{1}{\phi_i(\vec{r}_i)} \left[\frac{\hbar^2}{2\mu} \nabla^2 \phi_i(\vec{r}_i) \right] + \sum_{i=1}^2 \left[-\frac{Ze^2}{r_i} \left(e^{-\frac{r_i}{Za_0}} \right) + \frac{Ze^2 \vec{S}_i \cdot \vec{L}_i}{2m_i^2 c^2 r_i^3} - \frac{1}{c^2} \left[\frac{2}{3} g_s g_l \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S}_i \cdot \vec{I} \nabla^2 \left(\frac{1}{r_i} \right) \right] + \frac{\mu_B}{\hbar} (\vec{L}_i + 2\vec{S}_i) \cdot \vec{B} \right] = E_i$$

$i = [1, 2]$

As with any differential equation, if ϕ_1 and ϕ_2 are solutions to the equation, then any linear combinations of solutions must itself be a solution. Since electrons are fermions, antisymmetric solutions are needed. This is achieved by expressing the solution in terms of the Slater Determinant

$$\phi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_1(1) |\bar{S}_1(1)\rangle & \phi_2(1) |\bar{S}_2(1)\rangle \\ \phi_1(2) |\bar{S}_1(2)\rangle & \phi_2(2) |\bar{S}_2(2)\rangle \end{vmatrix}$$

Where $|\bar{S}_i\rangle; i = 1, 2$ is the spin for the corresponding function ϕ_i

Expanding, this

$$\text{yields } \phi(1,2) = \frac{1}{\sqrt{2}} \left[\phi_1(1) \phi_2(2) |\bar{S}_1(1)\rangle |\bar{S}_2(2)\rangle - \phi_2(1) \phi_1(2) |\bar{S}_2(2)\rangle |\bar{S}_1(1)\rangle \right].$$

There are now two options to allow $\phi(1,2)$ to be anti-symmetric. Either both electrons occupy the same orbital and the spinor becomes anti-symmetric

($\chi^A(1,2) = |\bar{S}_1(1)\rangle |\bar{S}_2(2)\rangle - |\bar{S}_2(2)\rangle |\bar{S}_1(1)\rangle$), or the electrons occupy different orbitals and the spinor is symmetric ($\chi^S(1,2) = |\bar{S}_1(1)\rangle |\bar{S}_2(2)\rangle + |\bar{S}_2(2)\rangle |\bar{S}_1(1)\rangle$). Thus, the two possibilities for $\phi(1,2)$ are

Electrons in same orbital ϕ :

$$\phi(1,2) = \frac{1}{\sqrt{2}} \chi^A(1,2) [\phi_\phi(1) \phi_\phi(2)]$$

Electrons in the same spin state ∂ :

$$\phi(1,2) = \frac{1}{\sqrt{2}} |\bar{S}_1(1)\rangle |\bar{S}_2(2)\rangle [\phi_1(1) \phi_2(2) - \phi_2(1) \phi_1(2)]$$

The expected energy values associated with each configuration are

$$\langle \varepsilon \rangle = \int \phi(1,2)^* \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] \phi(1,2) d\vec{r}$$

$$\begin{aligned} \langle \varepsilon \rangle &= \int (\phi_1(1)\phi_2(2) \pm \phi_2(1)\phi_1(2)) \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] (\phi_1(1)\phi_2(2) \pm \phi_2(1)\phi_1(2)) d\vec{r} \\ &= \int \left(\phi_1(1)\phi_2(2) \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] \pm \phi_2(1)\phi_1(2) \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] \right) (\phi_1(1)\phi_2(2) \pm \phi_2(1)\phi_1(2)) d\vec{r} \\ &= \int \left(\phi_1(1)\phi_2(2) \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] (\phi_1(1)\phi_2(2)) \pm \phi_2(1)\phi_1(2) \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] (\pm\phi_2(1)\phi_1(2)) \right) d\vec{r} \\ &= \int \left(\phi_1(1)^2 \phi_2(2) \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] (\phi_2(2)) + \phi_1(1)\phi_2(2)^2 \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] (\phi_1(1)) \right) d\vec{r} \pm \\ &\int \left(\phi_2(1)^2 \phi_1(2) \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] (\phi_1(2)) + \phi_2(1)\phi_1(2)^2 \left[-\frac{\hbar^2}{2m} \nabla_r^2 + V(\vec{r}) \right] (\phi_2(1)) \right) d\vec{r} \end{aligned}$$

And the corresponding probability density is expressed as

$$P(1,2) = \frac{1}{2} \left[\phi_1(1)^2 \phi_2(2)^2 + \phi_2(1)^2 \phi_1(2)^2 \pm 2\phi_1(1)\phi_2(2)\phi_2(1)\phi_1(2) \right]$$

As expected, the case of both particles existing in the same orbital causes an increase in the charge density as expressed by the interference term $2\phi_1(1)\phi_2(2)\phi_2(1)\phi_1(2)$.

The Multi Electron Atom

The results obtained from the 2-electron atom can be generalized quite easily to accommodate an atom with any number of electrons. The only considerations needed are for the interaction potentials. These include the standard Coulomb potential existing between each electron and the nucleus, the interaction potential between pairs of electrons, spin-spin interactions of both interparticle and particle-nuclei interactions, and spin orbit interactions. The only difficulty arises in the need to solve N Hydrogenic Schrödinger equations. For each electron, the spatial wave function $\phi_i(\vec{r}_i)$ will satisfy the equation

$$-\frac{1}{\phi_i(\vec{r}_i)} \left[\frac{\hbar^2}{2\mu} \nabla_i^2 \phi_i(\vec{r}_i) \right] + \sum_{i=1}^N \left[-\frac{Ze^2}{r_i} \left(e^{-\frac{r_i}{Za_0}} \right) + \frac{Ze^2 \vec{S}_i \cdot \vec{L}_i}{2m_i^2 c^2 r_i^3} - \frac{1}{c^2} \left[\frac{2}{3} g_s g_l \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S}_i \cdot \vec{I} \nabla^2 \left(\frac{1}{r_i} \right) \right] + \frac{\mu_B}{\hbar} (\vec{L}_i + 2\vec{S}_i) \cdot \vec{B} \right] = E_i$$

$i = [1, N]$

Thus, for Carbon, consisting of 6 electrons, there will be 6 such equations to solve:

$$\begin{aligned}
& -\frac{1}{\varphi_1(\vec{r}_1)} \left[\frac{\hbar^2}{2\mu} \nabla_1^2 \varphi_1(\vec{r}_1) \right] + \sum_{i=1}^6 \left[-\frac{6e^2}{r_1} \left(e^{-\frac{r_1}{6a_0}} \right) + \frac{6e^2 \vec{S}_1 \cdot \vec{L}_1}{2m^2 c^2 r_1^3} - \frac{1}{c^2} \left[\frac{2}{3} g_S g_I \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S}_1 \cdot \vec{I} \nabla^2 \left(\frac{1}{r_1} \right) \right] + \frac{\mu_B}{\hbar} (\vec{L}_1 + 2\vec{S}_1) \cdot \vec{B} \right] = E_1 \\
& -\frac{1}{\varphi_2(\vec{r}_2)} \left[\frac{\hbar^2}{2\mu} \nabla_2^2 \varphi_2(\vec{r}_2) \right] + \sum_{i=1}^6 \left[-\frac{6e^2}{r_2} \left(e^{-\frac{r_2}{6a_0}} \right) + \frac{6e^2 \vec{S}_2 \cdot \vec{L}_2}{2m^2 c^2 r_2^3} - \frac{1}{c^2} \left[\frac{2}{3} g_S g_I \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S}_2 \cdot \vec{I} \nabla^2 \left(\frac{1}{r_2} \right) \right] + \frac{\mu_B}{\hbar} (\vec{L}_2 + 2\vec{S}_2) \cdot \vec{B} \right] = E_2 \\
& \quad \vdots \\
& -\frac{1}{\varphi_6(\vec{r}_6)} \left[\frac{\hbar^2}{2\mu} \nabla_6^2 \varphi_6(\vec{r}_6) \right] + \sum_{i=1}^6 \left[-\frac{6e^2}{r_6} \left(e^{-\frac{r_6}{6a_0}} \right) + \frac{6e^2 \vec{S}_6 \cdot \vec{L}_6}{2m^2 c^2 r_6^3} - \frac{1}{c^2} \left[\frac{2}{3} g_S g_I \left(\frac{e}{2m_e} \right)^2 \frac{m_e}{M_p} \vec{S}_6 \cdot \vec{I} \nabla^2 \left(\frac{1}{r_6} \right) \right] + \frac{\mu_B}{\hbar} (\vec{L}_6 + 2\vec{S}_6) \cdot \vec{B} \right] = E_6
\end{aligned}$$

For which the spatial wave function of Carbon representing the set of six electrons will be of the form

$$\phi_{Carbon}(\vec{r}) = \phi_1 \phi_2 \phi_3 \phi_4 \phi_5 \phi_6$$

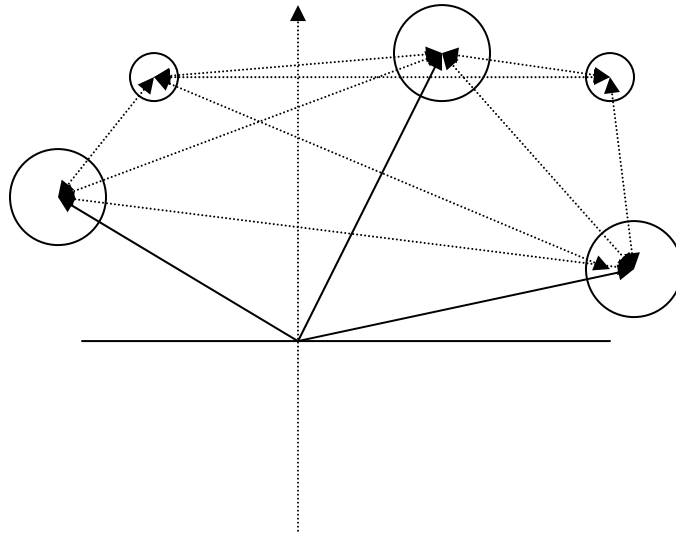
The argument is again made that any linear combination of $\phi_i; i = [1, 6]$ is also a solution to the Schrödinger equation. Thus, the Slater Determinant form of the solutions (including spin) is written as

$$\phi(1,2,3,4,5,6) = \frac{1}{\sqrt{6!}} \begin{vmatrix} \phi_1(1)\chi_1(1) & \phi_2(1)\chi_2(1) & \phi_3(1)\chi_3(1) & \phi_4(1)\chi_4(1) & \phi_5(1)\chi_5(1) & \phi_6(1)\chi_6(1) \\ \phi_1(2)\chi_1(2) & \phi_2(2)\chi_2(2) & \phi_3(2)\chi_3(2) & \phi_4(2)\chi_4(2) & \phi_5(2)\chi_5(2) & \phi_6(2)\chi_6(2) \\ \phi_1(3)\chi_1(3) & \phi_2(3)\chi_2(3) & \phi_3(3)\chi_3(3) & \phi_4(3)\chi_4(3) & \phi_5(3)\chi_5(3) & \phi_6(3)\chi_6(3) \\ \phi_1(4)\chi_1(4) & \phi_2(4)\chi_2(4) & \phi_3(4)\chi_3(4) & \phi_4(4)\chi_4(4) & \phi_5(4)\chi_5(4) & \phi_6(4)\chi_6(4) \\ \phi_1(5)\chi_1(5) & \phi_2(5)\chi_2(5) & \phi_3(5)\chi_3(5) & \phi_4(5)\chi_4(5) & \phi_5(5)\chi_5(5) & \phi_6(5)\chi_6(5) \\ \phi_1(6)\chi_1(6) & \phi_2(6)\chi_2(6) & \phi_3(6)\chi_3(6) & \phi_4(6)\chi_4(6) & \phi_5(6)\chi_5(6) & \phi_6(6)\chi_6(6) \end{vmatrix}$$

Molecules

The motion of the electron (to first approximation) is determined by “stationary” nuclei (i.e. electrons move much faster compared to the nuclei). The total energy of the system consists of electronic energy, which is a function of nuclear coordinates $\xi(\bar{R}_1, \bar{R}_2, \dots)$, together with the Coulomb repulsion between the nuclei, which also depends

$$\text{on } \bar{R}_i. V_c = e^2 \sum_{i=1}^{N-1} \sum_{j \neq i}^N \frac{1}{|\bar{R}_i - \bar{R}_j|}$$

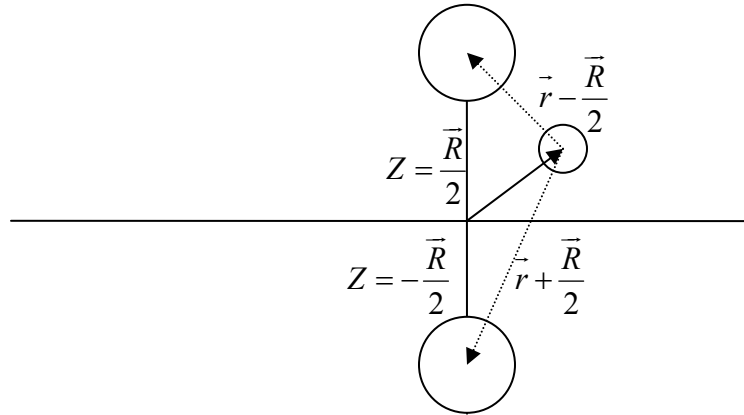


The set of position coordinates \bar{R}_i which minimizes the total energy yield a first approximation to the structure of the molecule. The nuclei sit in potential wells created by rapidly moving electrons and the other nuclei.

These wells allow motion about the equilibrium positions. When the electronic structure isn't in the ground state, the nuclei sit in a new set of potential wells and the motion is different.

The main task is to find an expression for the total energy, and minimize it to obtain a set of equilibrium positions

Diatomic Molecules



It is acceptable to assume the nuclei are fixed (since the nucleus accounts for 99% of the atomic mass, and has little motion compared to the electrons), so only the electronic wave function $\psi_e(\vec{r})$ needs consideration.

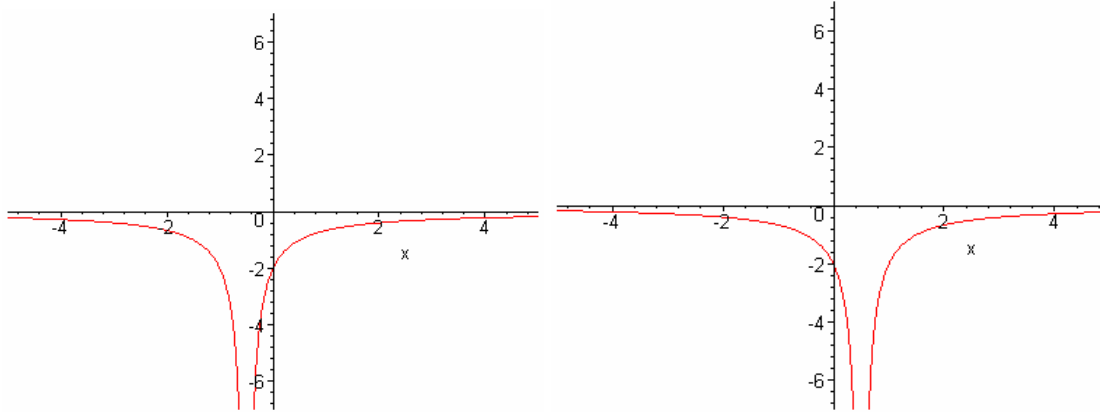
$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_e^2 - k \frac{e^2}{\left| \vec{r} + \frac{\bar{R}}{2} \right|} - k \frac{e^2}{\left| \vec{r} - \frac{\bar{R}}{2} \right|} + k \frac{e^2}{R} \right\} \psi_e(\vec{r}) = \varepsilon_e \psi_e(\vec{r})$$

The H_2^+ Molecule

The electron-proton interaction potential appears as below. It should be noted that the function consists of 2 potential wells, each of which behave in a similar fashion to the ground state Hydrogen atom. Such a potential is of the form

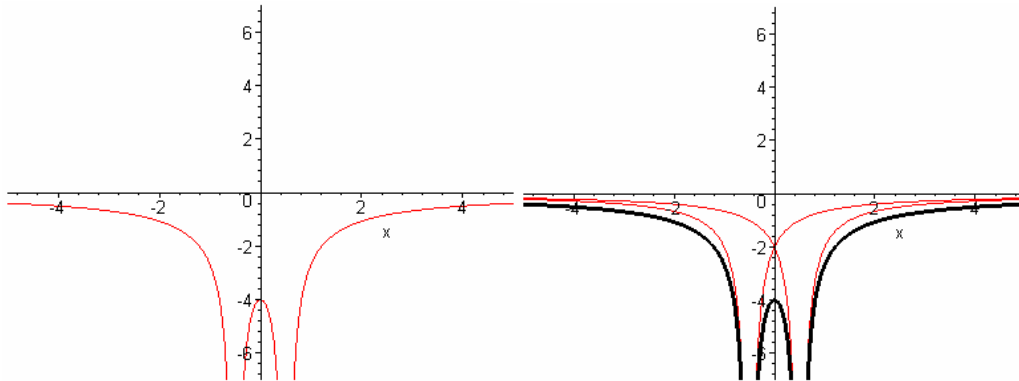
$$V = -\frac{e^2}{\left| \vec{r} - \bar{R} \right|}$$

With \bar{R} denoting the position of the nucleus. Thus, the potential is a superposition of Hydrogenic potentials; one solution having the nucleus at $\frac{\bar{R}}{2}$, the other with the nucleus at $-\frac{\bar{R}}{2}$.



$$V = -\frac{e^2}{\left| \vec{r} + \frac{\vec{R}}{2} \right|}$$

$$V = -\frac{e^2}{\left| \vec{r} - \frac{\vec{R}}{2} \right|}$$



In the regions close to $\pm \frac{\vec{R}}{2}$, the Hydrogenic potentials are excellent approximations, and so it is expected that the wave function in those regions will resemble the ground state Hydrogenic solutions. Thus, the normalized molecular wave functions for the ground state molecule can be approximated by:

Symmetric Wave Function:

$$\psi^+(\vec{r}) = \frac{1}{\sqrt{2}} \left(\phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) + \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \right)$$

Anti-symmetric Wave Function:

$$\psi^-(\vec{r}) = \frac{1}{\sqrt{2}} \left(\phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) - \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \right)$$

The average energy associated with these functions is given by

$$\begin{aligned} \xi_{\pm} &= \frac{1}{2} \int \left(\phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \pm \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \right) \left[-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{\left| \vec{r} - \frac{\vec{R}}{2} \right|} - \frac{e^2}{\left| \vec{r} + \frac{\vec{R}}{2} \right|} + \frac{e^2}{R} \right] \left(\phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \pm \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \right) d\vec{r} \\ \xi_{\pm} &= \left\{ \frac{1}{2} \int \left(\phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \pm \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \right) \left[\left(-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{\left| \vec{r} - \frac{\vec{R}}{2} \right|} \right) \phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \pm \left(-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{e^2}{\left| \vec{r} + \frac{\vec{R}}{2} \right|} \right) \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \right] d\vec{r} \right\} \mathbf{I} \\ &+ \left\{ \frac{1}{2} \int \phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right)^2 \left(-\frac{e^2}{\left| \vec{r} + \frac{\vec{R}}{2} \right|} + \frac{e^2}{R} \right) d\vec{r} + \frac{1}{2} \int \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right)^2 \left(-\frac{e^2}{\left| \vec{r} - \frac{\vec{R}}{2} \right|} + \frac{e^2}{R} \right) d\vec{r} \right\} \mathbf{II} \\ &\pm \left\{ \frac{1}{2} \int \phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \left(-\frac{e^2}{\left| \vec{r} - \frac{\vec{R}}{2} \right|} + \frac{e^2}{R} \right) \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) d\vec{r} \pm \frac{1}{2} \int \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \left(-\frac{e^2}{\left| \vec{r} + \frac{\vec{R}}{2} \right|} + \frac{e^2}{R} \right) \phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) d\vec{r} \right\} \mathbf{III} \end{aligned}$$

I yields the average Hydrogenic ground state energy ζ_{H1s} , **II** yields the average electron-nuclei interaction, and **III** is the quantum interference term allowing for the possibility of the electron to be found around either of the two nuclei.

$$\text{Letting } G = \int \phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right)^2 \left(-\frac{e^2}{\left| \vec{r} + \frac{\vec{R}}{2} \right|} + \frac{e^2}{R} \right) d\vec{r}$$

$$\text{And } S = \int \phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \left(-\frac{e^2}{\left| \vec{r} - \frac{\vec{R}}{2} \right|} + \frac{e^2}{R} \right) \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) d\vec{r}$$

Thus, the average energy can be expressed as

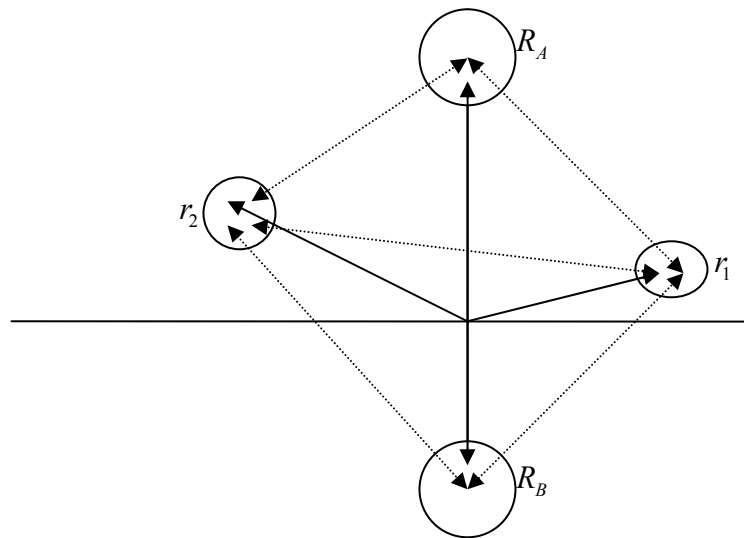
$$\zeta_{\pm} = \zeta_{H1s} + G \pm S$$

The overlap integral S is responsible for the binding energy in the molecule. The probability density distribution of the molecule is

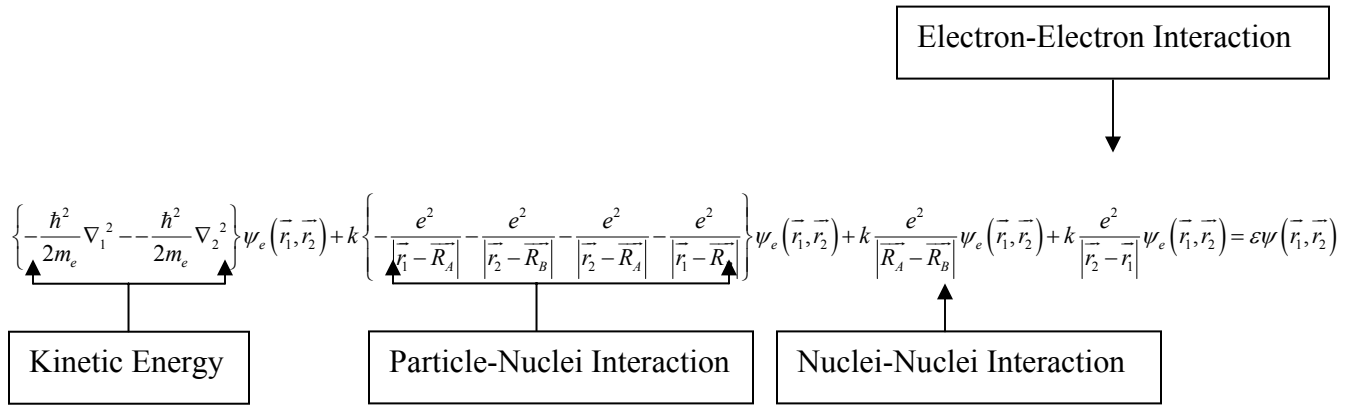
$$|\psi_{\pm}|^2 = \frac{1}{2} \left[\left| \phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \right|^2 + \left| \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \right|^2 \pm 2 \phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right) \right]$$

The $2\phi_{H1s} \left(\vec{r} - \frac{\vec{R}}{2} \right) \phi_{H1s} \left(\vec{r} + \frac{\vec{R}}{2} \right)$ term indicates an excess of negative charge existing between the two nuclei. This acts to partially shield the proton-proton repulsion, and partially attracts each of the nuclei towards the charge cloud.

2 Electron Molecules



The situation of a diatomic molecule consisting of 2 electrons is slightly more intricate than for the H_2^+ molecule. The interaction potentials for electron-electron repulsion must be considered, as well as the Coulomb interaction with the nuclei. The Schrödinger equation in this case must be



$$\psi_i(\vec{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

Symmetric Wave Function:

$$\psi_e^+(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{N}} \left(\psi_A(\vec{r}_1) \psi_B(\vec{r}_2) + \psi_A(\vec{r}_2) \psi_B(\vec{r}_1) \right)$$

Anti-symmetric Wave Function:

$$\psi_e^-(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{N}} \left(\psi_A(\vec{r}_1) \psi_B(\vec{r}_2) - \psi_A(\vec{r}_2) \psi_B(\vec{r}_1) \right)$$

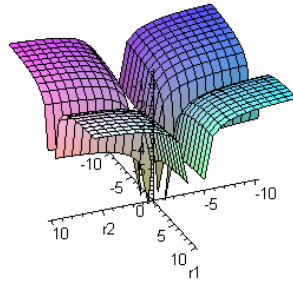
The appropriate solution depends on the spin of the electrons. The total wave function including spin must be antisymmetric under the interchange of the electrons. If the total spin of the electrons is zero, the wave function is antisymmetric, so the spatial wave function must be symmetric (i.e. $\psi_e^+(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{N}} \left(\psi_A(\vec{r}_1) \psi_B(\vec{r}_2) + \psi_A(\vec{r}_2) \psi_B(\vec{r}_1) \right)$).

The H₂ Molecule

The interaction potential between the electrons and the two nuclei of the molecule is described by

$$V_{NE} = -\frac{e^2}{\left| \vec{r}_1 - \frac{\vec{R}}{2} \right|} - \frac{e^2}{\left| \vec{r}_2 - \frac{\vec{R}}{2} \right|} - \frac{e^2}{\left| \vec{r}_1 + \frac{\vec{R}}{2} \right|} - \frac{e^2}{\left| \vec{r}_2 + \frac{\vec{R}}{2} \right|}$$

Where $\vec{r}_i; i = [1, 2]$ are the positions of the electrons, and the nuclei are located at $\pm \frac{\vec{R}}{2}$.



The potential wells present in this interaction are similar to that of the ground state Hydrogenic atom, whose wave function was given as

$$\phi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_1(1)\chi_1(1) & \phi_2(1)\chi_2(1) \\ \phi_1(2)\chi_1(2) & \phi_2(2)\chi_2(2) \end{vmatrix}$$

Let ϕ_1 be the ground state function for the nucleus at $\frac{\bar{R}}{2}$ and ϕ_2 the ground state function for the other at $-\frac{\bar{R}}{2}$. Thus, the Slater determinant for the molecule can be written as

$$\phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}\left(\bar{r}_1 - \frac{\bar{R}}{2}\right)\chi_1(1) & \phi_{1s}\left(\bar{r}_2 - \frac{\bar{R}}{2}\right)\chi_2(1) \\ \phi_{1s}\left(\bar{r}_1 + \frac{\bar{R}}{2}\right)\chi_1(2) & \phi_{1s}\left(\bar{r}_2 + \frac{\bar{R}}{2}\right)\chi_2(2) \end{vmatrix}$$

Expanding, this gives

$$\phi(1,2) = \frac{1}{\sqrt{2}} \left[\phi_{1s}\left(\bar{r}_1 - \frac{\bar{R}}{2}\right)\phi_{1s}\left(\bar{r}_2 + \frac{\bar{R}}{2}\right)\chi(1,2) - \phi_{1s}\left(\bar{r}_2 - \frac{\bar{R}}{2}\right)\phi_{1s}\left(\bar{r}_1 + \frac{\bar{R}}{2}\right)\chi(2,1) \right]$$

Since both electrons occupy the 1s orbital, an anti-symmetric spinor $\chi^A(1,2)$ is required so that

$$\phi(1,2) = \frac{1}{\sqrt{2}} \chi^A(1,2) \left[\phi_{1s}\left(\bar{r}_1 - \frac{\bar{R}}{2}\right)\phi_{1s}\left(\bar{r}_2 + \frac{\bar{R}}{2}\right) + \phi_{1s}\left(\bar{r}_2 - \frac{\bar{R}}{2}\right)\phi_{1s}\left(\bar{r}_1 + \frac{\bar{R}}{2}\right) \right]$$

The probability density

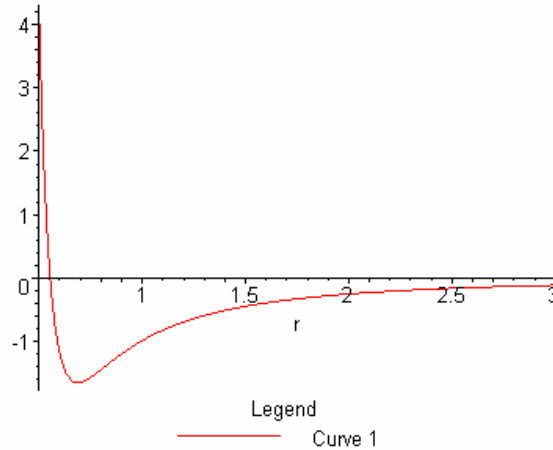
$$P = \frac{1}{2} \left[\phi_{1s} \left(\bar{r}_1 - \frac{\bar{R}}{2} \right)^2 \phi_{1s} \left(\bar{r}_2 + \frac{\bar{R}}{2} \right)^2 + \phi_{1s} \left(\bar{r}_2 - \frac{\bar{R}}{2} \right)^2 \phi_{1s} \left(\bar{r}_1 + \frac{\bar{R}}{2} \right)^2 + 2\phi_{1s} \left(\bar{r}_1 - \frac{\bar{R}}{2} \right) \phi_{1s} \left(\bar{r}_2 + \frac{\bar{R}}{2} \right) \phi_{1s} \left(\bar{r}_2 - \frac{\bar{R}}{2} \right) \phi_{1s} \left(\bar{r}_1 + \frac{\bar{R}}{2} \right) \right]$$

indicates this is a desirable wave function, since the presence of the interference term

$$2\phi_{1s} \left(\bar{r}_1 - \frac{\bar{R}}{2} \right) \phi_{1s} \left(\bar{r}_2 + \frac{\bar{R}}{2} \right) \phi_{1s} \left(\bar{r}_2 - \frac{\bar{R}}{2} \right) \phi_{1s} \left(\bar{r}_1 + \frac{\bar{R}}{2} \right)$$

implies there is a region of increased charge density between the two nuclei. This is responsible for the covalent bonding in the singlet case.

Determining the Energy



At large separations, the Coulomb potential is dominant, since electrons far away from the nuclei will be attracted. There is another repulsive potential present at small distances, which exists between the 2 ions.

The potential energy of a H_2^+ molecule is approximated by

$$V = -k \frac{e^2}{\left(R + \frac{e^2}{54.4eV} \right)} + \frac{b}{R^9} - 13.6eV$$

↖ Repulsion
↗ Coulomb

To get this, 2 limits must be considered: for small separations ($r \rightarrow 0$), the H_2 molecule is essentially an He^+ atom. Using $E = \left(\frac{Z}{n}\right)^2 (-13.6eV)$, the binding energy is $-54.4 eV$, so $\lim_{r \rightarrow 0} V(r) = -54.4eV$. However, there must also be an infinite repulsion between the 2 protons at small distances, accounting for the $\frac{b}{R^9}$ term. At large separations ($r \rightarrow \infty$) the 2 nuclei are isolated, creating in effect an isolated H atom with energy $-13.6 eV$,

so $\lim_{r \rightarrow \infty} V(r) = -13.6eV$. In general, for any molecule, the potential can be approximated by

$$V = -k \left[\frac{e^2}{R + \left(\lim_{R \rightarrow 0} \left(\left(\frac{Z(R)}{n} \right)^2 (-13.6eV) \right) \right)} \right] + \frac{b}{R^9} + \lim_{R \rightarrow \infty} \left(\left(\frac{Z(R)}{n} \right)^2 (-13.6eV) \right)$$

neglecting P^+P^+ repulsion

Vibrations in Molecules

Maintaining the nuclei in the lowest energy state, consider next the possible motions with a given electronic cloud. The discussion will be limited to diatomic molecules. Vibrations shall be discussed first.

The Morse Potential for a vibrating molecule is expressed as

$$V(R) = A \left(e^{-2a(R-R_0)} - 2e^{-a(R-R_0)} \right)$$

In the first approximation, the nuclei are located at fixed positions with separation determined by the minimum of the electronic + Coulomb energy:

$$V(R) = \xi(R) + \frac{Z_1 Z_2}{R}$$

Using a Taylor expansion about the equilibrium spacing R_o , the potential in the first approximation is

$$V(R) = V(R_o) + (R - R_o) \frac{dV}{dR} + \frac{1}{2} (R - R_o)^2 \frac{d^2V}{dR^2}.$$

Knowing that at the equilibrium spacing, the potential is minimized $\left(\frac{dV}{dR} = 0\right)$, we get

$$V(R) = V(R_o) + \frac{1}{2} (R - R_o)^2 \frac{d^2V}{dR^2}$$

or

Harmonic
Oscillator
Potential $\rightarrow V(R) = V(R_o) + \frac{1}{2} (R - R_o)^2 \left(2 \frac{Z_1 Z_2 e^2}{R^3} \right)$

$$\omega = \sqrt{\frac{K}{\mu_{\text{reduced}}}}$$

↑
"Spring
Constant" K

So, in the equilibrium separation, the potential is harmonic and the spectrum of one-dimensional vibrational motion is the familiar simple harmonic oscillator spectrum

$$E_v = \left(v + \frac{1}{2} \right) \hbar \omega$$

$$(E_{\text{vib}} \approx 100 \text{meV})$$

Rotation of Molecules

Molecules can also rotate as rigid bodies. The spectrum for a spherical body is given by the eigenvalues of the operator

$$H_{\text{rot}} = \frac{L^2}{2I} = E_{\text{rot}}$$

Here, it is assumed that the molecule rotates in a similar fashion to a rigid dumbbell. Recalling for such a system the moment of inertia is $I = \mu_{\text{reduced}} R^2$, and using quantization of angular momentum,

$$E_{\text{rot}} = \frac{\hbar^2}{2\mu_{\text{reduced}}} \left(\frac{J(J+1)}{R_o^2} \right)$$

$$(E_{rot} \approx 1meV)$$

Modelling the CH₄ Molecule

The Methane molecule consists of a single Carbon atom surrounded by 4 Hydrogen atoms. Both species of atoms have been discussed previously. Let \overline{R}_C represent the position of the Carbon nucleus, and $\overline{R}_{H1}, \overline{R}_{H2}, \overline{R}_{H3}, \overline{R}_{H4}$ be the positions of the 4 Hydrogen nuclei. Thus, the electron-nuclei interaction potential will appear as

$$V_{NE} = -\frac{e^2}{|\overline{r}_1 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_1 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_1 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_2 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_2 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_2 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_3 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_3 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_3 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_4 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_4 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_4 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_5 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_5 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_5 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_6 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_6 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_6 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_7 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_7 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_7 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_8 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_8 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_8 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_9 - \overline{R}_C|} - \frac{e^2}{|\overline{r}_9 - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_9 - \overline{R}_{H2}|} - \frac{e^2}{|\overline{r}_{10} - \overline{R}_C|} - \frac{e^2}{|\overline{r}_{10} - \overline{R}_{H1}|} - \frac{e^2}{|\overline{r}_{10} - \overline{R}_{H2}|}$$

The nuclei-nuclei potential will be of the form

$$V_{NN} = \frac{e^2}{|\overline{R}_C - \overline{R}_{H1}|} + \frac{e^2}{|\overline{R}_C - \overline{R}_{H2}|} + \frac{e^2}{|\overline{R}_C - \overline{R}_{H3}|} + \frac{e^2}{|\overline{R}_C - \overline{R}_{H4}|} + \frac{e^2}{|\overline{R}_{H2} - \overline{R}_{H1}|} + \frac{e^2}{|\overline{R}_{H3} - \overline{R}_{H1}|} + \frac{e^2}{|\overline{R}_{H4} - \overline{R}_{H1}|} + \frac{e^2}{|\overline{R}_{H2} - \overline{R}_{H3}|} + \frac{e^2}{|\overline{R}_{H2} - \overline{R}_{H4}|} + \frac{e^2}{|\overline{R}_{H3} - \overline{R}_{H4}|}$$

And the electron-electron repulsion will appear as

$$\begin{aligned}
 V_{EE} = & \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_3|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_4|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_5|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_6|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_7|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_8|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_9|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_{10}|} + \\
 & \frac{e^2}{|\vec{r}_2 - \vec{r}_3|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_4|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_5|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_6|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_7|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_8|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_9|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_{10}|} + \\
 & \frac{e^2}{|\vec{r}_3 - \vec{r}_4|} + \frac{e^2}{|\vec{r}_3 - \vec{r}_5|} + \frac{e^2}{|\vec{r}_3 - \vec{r}_6|} + \frac{e^2}{|\vec{r}_3 - \vec{r}_7|} + \frac{e^2}{|\vec{r}_3 - \vec{r}_8|} + \frac{e^2}{|\vec{r}_3 - \vec{r}_9|} + \frac{e^2}{|\vec{r}_3 - \vec{r}_{10}|} + \\
 & \frac{e^2}{|\vec{r}_4 - \vec{r}_5|} + \frac{e^2}{|\vec{r}_4 - \vec{r}_6|} + \frac{e^2}{|\vec{r}_4 - \vec{r}_7|} + \frac{e^2}{|\vec{r}_4 - \vec{r}_8|} + \frac{e^2}{|\vec{r}_4 - \vec{r}_9|} + \frac{e^2}{|\vec{r}_4 - \vec{r}_{10}|} + \\
 & \frac{e^2}{|\vec{r}_5 - \vec{r}_6|} + \frac{e^2}{|\vec{r}_5 - \vec{r}_7|} + \frac{e^2}{|\vec{r}_5 - \vec{r}_8|} + \frac{e^2}{|\vec{r}_5 - \vec{r}_9|} + \frac{e^2}{|\vec{r}_5 - \vec{r}_{10}|} + \\
 & \frac{e^2}{|\vec{r}_6 - \vec{r}_7|} + \frac{e^2}{|\vec{r}_6 - \vec{r}_8|} + \frac{e^2}{|\vec{r}_6 - \vec{r}_9|} + \frac{e^2}{|\vec{r}_6 - \vec{r}_{10}|} + \\
 & \frac{e^2}{|\vec{r}_7 - \vec{r}_8|} + \frac{e^2}{|\vec{r}_7 - \vec{r}_9|} + \frac{e^2}{|\vec{r}_7 - \vec{r}_{10}|} + \\
 & \frac{e^2}{|\vec{r}_8 - \vec{r}_9|} + \frac{e^2}{|\vec{r}_8 - \vec{r}_{10}|} + \\
 & \frac{e^2}{|\vec{r}_9 - \vec{r}_{10}|}
 \end{aligned}$$

Interactions amongst the spins and angular momenta of the 10 electrons and 4 nuclei must also be considered. Let \vec{I}_C be the total spin of the Carbon atom and $\vec{I}_{H_i}; i = [1, 4]$ be the total spin of the 4 Hydrogen atoms. The orbital angular momenta and spins of the electrons will be denoted by \vec{L}_i and $\vec{S}_i; i = [1, 10]$ respectively.