Idea: Real materials are composed of many identical electrons. In general, describing these electrons accurately, using the laws of quantum mechanics, is mathematically very difficult. In this project, we will study a model many-electron system for which the mathematics is tractable. This will enable us to draw some general conclusions about the behavior of many-electron systems and to access some mathematical and computational methods for studying them.

Prerequisites: Elementary quantum mechanics (PHY 141 or CHM 342/344), Differential equations (MTH 251), and some computer programing experience and interest.

Dates: The starting date is flexible. Summer of 2000 would be ideal.

Some details of idea

We can write Schrödinger Equation for a many electron system as follows:

\[ \mathcal{H}\Psi_\alpha = E_\alpha \Psi_\alpha, \]

where,

\[ \mathcal{H} = \sum_i \left( -\frac{\hbar^2}{2m} \nabla_i^2 + V(\mathbf{r}_i) \right) + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \]

and

\[ \Psi_\alpha(x_1, x_2, x_3, ... x_N) = -\Psi_\alpha(x_2, x_1, x_3, ... x_N). \]

Energy eigenvalue of this Hamiltonian can be expressed as an expectation value:

\[ E_\alpha = \langle \Psi_\alpha | \mathcal{H} | \Psi_\alpha \rangle = \int d1 \int d2 \int d3 \ldots \int dN \Psi_\alpha^* \mathcal{H} \Psi_\alpha, \]

which can be written and a very suggestive form:

\[ \Rightarrow E_\alpha = \text{Trace} \left\{ \rho_\alpha \mathcal{K} \right\}. \]

Here, the “reduced” or “pair” Hamiltonian is defined according to:

\[ \mathcal{K}(1, 2) \equiv \left( \frac{1}{N-1} \right) (h(1) + h(2)) + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \]
and the two-particle density matrix is given by:
\[
\rho^2 _{\alpha} (1, 2; 1', 2') \equiv \int d3 \int d4 \ldots \int dN \Psi_\alpha (1, 2, 3, 4 \ldots N) \Psi_\alpha (1', 2', 3, 4 \ldots N)
\]

Consider, more carefully, the pair Hamiltonian:
\[
\mathcal{K}(1, 2) \equiv \left( \frac{1}{N - 1} \right) (h(1) + h(2)) + \frac{e^2}{|r_1 - r_2|}
\]

Suppose that it is possible to find the eigenvalues \( \varepsilon_n \) and corresponding eigenstates \( |n\rangle \):
\[
\mathcal{K}|n\rangle = \varepsilon_n |n\rangle.
\]

The eigenstates \( E_\alpha \) of the many-electron system can be expressed in terms a pair states state expansion:
\[
\Rightarrow E_\alpha = \sum_n \varepsilon_n W_n^\alpha
\]
where \( W_n^\alpha \equiv \langle n | \rho^2 _{\alpha} | n \rangle \) and \( \sum_n W_n^\alpha = 1 \).

**Proposed project:** Systematic study of the pair state expansion for many-electron “harmonic” atoms.

**real atom:** \( V(r_1) = \frac{-Ze^2}{r_1} \) \Rightarrow “harmonic” atom: \( V(r_1) = \frac{1}{2} Kr_1^2 \).

The “harmonic” atom model is useful because:

- \( \mathcal{K}|n\rangle = \varepsilon_n |n\rangle \) can be solved **exactly**!
- \( \rho^2 _{\alpha} \) can be approximated using techniques developed by quantum chemists.

Some **questions** to be answered as we study \( E_\alpha = \sum_n \varepsilon_n W_n^\alpha \) for increasing numbers of identical electrons, \( N \), in our model system:

- Is there an approximate shell structure for our “harmonic” atoms as there is for the periodic table of real atoms?
- Are there only a small number of pair states participating in the states of the “harmonic” atoms? That is, is it true that \( W_n^\alpha \approx 0 \) for \( n > N(N - 1)/2 \)?