## New Project for Undergraduate or MS Student
## Pair Hamiltonian analysis of a many-electron problem

**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,

$$\mathcal{H} \equiv \sum_i \underbrace{\left( -\frac{\hbar^2}{2m}\nabla_i^2 + V(\mathbf{r}_i) \right)}_{h(i)} + \sum_{i<j} \frac{e^2}{|\mathbf{r_i} - \mathbf{r_j}|}$$

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 expection value:

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

**which can be written and a very suggestive form:**

$$\Rightarrow \mathbf{E}_\alpha = \text{Trace}\left\{ \rho_\alpha^{\mathbf{2}} \, \mathcal{K} \right\}.$$

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:

$$\rho^2_\alpha(1,2;1',2') \equiv \int d3 \int d4 \ldots \int dN \Psi^*_\alpha(1,2,3,4...N)\Psi_\alpha(1',2',3,4...N)$$

Consider, more carefully, the pair Hamiltonian:

$$\mathcal{K}(1,2) \equiv \left(\frac{1}{N-1}\right)(h(1)+h(2)) + \frac{e^2}{|\mathbf{r_1}-\mathbf{r_2}|}$$

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:

$$\Rightarrow \mathbf{E}_\alpha = \sum_{\mathbf{n}} \varepsilon_{\mathbf{n}} \mathbf{W}^\alpha_{\mathbf{n}}$$

$$\text{where} \quad W^\alpha_n \equiv \langle n|\rho^2_\alpha|n\rangle \ \text{ and } \ \sum_n W^\alpha_n = 1.$$

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

$$\text{real atom: } V(r_1) = \frac{-Ze^2}{r_1} \quad \Rightarrow \quad \text{"harmonic" atom: } V(r_1) = \frac{1}{2}K_Z r_1^2.$$

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 $E_\alpha = \sum_n \varepsilon_n W^\alpha_n$ 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 $W^\alpha_n \approx 0$ for $n > N(N-1)/2$ ?