1. Introduction

Textbook (Fetters & Walecka, p. 3): "The physical world consists of interacting many-particle systems"

Examples of (non-relativistic) quantum many-particle systems:

- atoms (Z = 120)
- molecules/quantum chemistry (N \approx 10 - 10^5)
- condensed matter (N = 10^{23} / \text{cm}^3 in bulk material; \sim 10^2 electrons per "unit cell" of periodic lattice)
- atomic nuclei (N \leq 300)
- neutron stars (s_0 \approx 0.14 \text{fm}^{-3} \Rightarrow N \approx 10^{38} / \text{cm}^3)

Structure of N-particle Hamiltonian

To determine H = E for N particles, it is useful to start from the expression for the total energy of a classical N-particle system (see Goldstein, chapters 1). We assume the particles interact via two-body forces

\[ \hat{F}^{(2)}(\hat{r}_i, \hat{r}_j) \leftrightarrow V^{(2)}(\hat{r}_i, \hat{r}_j) \]

2-body force 2-body interaction
In addition, the system may experience an external force field
\[ \mathbf{F}_{\text{ext}}(\mathbf{r}_i) \leftrightarrow V_{\text{ext}}(\mathbf{r}_i) \]
Assuming conservative forces, one finds that the total energy \( E \) of this system is a constant of motion:
\[
E = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i,j=1}^{N} V^{(2)}(\mathbf{r}_i, \mathbf{r}_j)
\]
The quantization of this expression is straightforward. In coordinate space, we have

<table>
<thead>
<tr>
<th>classical</th>
<th>quantum</th>
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<tbody>
<tr>
<td>( \mathbf{r}_i )</td>
<td>( \hat{\mathbf{r}}_i \equiv \mathbf{r}_i )</td>
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<tr>
<td>( \mathbf{p}_i )</td>
<td>( \hat{\mathbf{p}}_i = -\mathbf{i} \hbar \nabla \mathbf{r}_i )</td>
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and we put \( E = H = \text{Hamiltonian function} \Rightarrow \text{quantum Hamiltonian} \ \hat{H} : \)
\[
\hat{H} = \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m_i} \nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i,j=1}^{N} V^{(2)}(\mathbf{r}_i, \mathbf{r}_j)
\]
Let us now consider a specific example, the \( N \)-electron atom.
Example 1: $N$-electron atom

The electrons are point particles of mass $m_e$ and electric charge $-e$. We model the atomic nucleus as a point particle of charge $(+Ze)$. This is a fairly good approximation (except for very heavy atoms) because the nuclear size is of order $R_N \approx fm = 10^{-15}m$, whereas the "orbital radius" of the electron is of order $R_e \approx \hbar = 10^{-10}m$. The atomic Hamiltonian has the structure (we use Coulomb potential in Gaussian units):

$$H_{\text{atom}} = H^0 + H^1$$

$$H^0 = \sum_{i=1}^{N} \left( -\frac{\hbar^2 \nabla_i^2}{2m_e} - \frac{Z e^2}{|\mathbf{r}_i|} \right) + \frac{1}{2} \sum_{i \neq j=1}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- kinetic energy of electrons
- electron-nucleus attraction
- electron-electron repulsion

Note that $H^0$ is independent of the spin of the electrons and nucleus. There are, of course, spin-dependent terms (all of which we will put into the Hamiltonian $H^1$). Fortunately, these terms are small and can be treated by perturbation theory in atomic physics. The most important spin-dep. term (which can be derived from the non-rel. limit of the Dirac Hamiltonian) is
The spin-orbit interaction (Shankar, QM, ch.17, p.468):

\[ H' \text{ (spin-orbit)} = \sum_{i=1}^{N} f(r_i) \hat{\mathbf{L}}_i^{(e)} \cdot \hat{\mathbf{S}}_i^{(e)} \]

where \( \hat{\mathbf{L}}_i^{(e)} \) is the orbital angular momentum operator for electron \( i \):

\[ \hat{\mathbf{L}}_i^{(e)} = \hat{\mathbf{r}}_i \times (-i\hbar \nabla_i) \]

and \( \hat{\mathbf{S}}_i^{(e)} \) is the spin operator for electron \( i \), given in terms of Pauli matrices \( \hat{\sigma}^{(e)}_x \):

\[ \hat{\mathbf{S}}_i^{(e)} = \frac{\hbar}{2} \hat{\sigma}^{(e)}_x \]

This spin-orbit term gives rise to the "fine-structure" splitting in atoms.

Taking spin into account, the atomic degrees of freedom are

|\begin{vmatrix} x_i \\ \vdots \end{vmatrix}| \equiv (\hat{\mathbf{r}}_i, S_i = \frac{1}{2}, S_z(i) = \pm \frac{1}{2})

all

coordinate

spin

of electrons

Significance of spin quantum number of electron:

\[ |\hat{S}| \leq \frac{\hbar}{2\sqrt{3}} \sqrt{s(s+1)}, \quad S = \frac{1}{2} \]

\[ |\hat{S}| \leq \frac{\hbar}{2\sqrt{2}} \sqrt{s(s+1)}, \quad S = \frac{3}{2} \]

and \( S_z = \pm \frac{1}{2} \)

Another spin-dep. term in \( H' \) is the interaction between
The electron magnetic moment $\hat{\mu}_{e}^{(e)}$ and the nuclear magnetic moment $\hat{\mu}_{n}^{(N)}$ which in many cases is non-zero (for "odd-even" nuclei); this interaction is strong and gives rise to the "hyperfine" splitting of atomic levels (see Shankar, QM, chapters 15, p. 407).

\[ H^1 (\text{hyperfine}) \propto \sum_{i=1}^{N} \hat{\mu}_{n}^{(N)} \cdot \hat{\mu}_{e}^{(e)} \]
\[ \propto \sum_{i=1}^{N} \hat{S}_{n}^{(N)} \cdot \hat{S}_{e}^{(e)} \]

So when we look at the structure of the atomic Hamiltonian, we see that there are two basic types of operators:

\[ \sum_{i=1}^{N} A(x_{i}) = \text{one-body operator} = A^{(1)} \]

Examples: kinetic energy, electron-nucleus interaction, spin-orbit term and hyperfine interaction.

\[ \frac{1}{2} \sum_{i\neq j}^{N} B(x_{i}, x_{j}) = \text{two-body operator} = B^{(2)} \]

Example: electron-electron Coulomb repulsion.

Time-dep. Schrödinger's eq. for N-particle systems

One postulates that the Schrödinger's eq. has the structure...
\[
[H \text{ atom } (x_1, x_2, \ldots, x_N) - \frac{i}{\hbar} \frac{\partial}{\partial t}] \psi(x_1, x_2, \ldots, x_N; t) = 0
\]

or in detail
\[
\left\{ \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{2e^2}{|r_i|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + H' (\text{spin-orbit}) + H' (\text{hyperfine}) + \ldots - \frac{i}{\hbar} \frac{\partial}{\partial t} \right\} \psi(\vec{r}_1, s_z^{(1)}; \vec{r}_2, s_z^{(2)}; \ldots; \vec{r}_N, s_z^{(N)}; t) = 0
\]

Now we can easily see why the solution of the \textit{N-}body quantum problem is difficult: the \textit{N-}body time-dep. Schrödinger's eq. is a time-dep. partial differential eq., which

- involves \textit{N} Laplacians \( \nabla_1^2, \nabla_2^2, \ldots, \nabla_N^2 \)
- depends on a total of \( 4N \) coordinates \((\vec{r}_i, s_z^{(i)})\)

\[ \Rightarrow \text{intelligent approximations to quantum many-body problem are necessary?} \]

Example 2: Molecular physics, quantum chemistry, condensed matter physics.

The main difference is that we have many nuclei/positive ions plus electrons.
The structure of the Hamiltonian is

$$H_{\text{cond. matter}} = \{ T_e^- + V_{e-N} \}$$

$$+ V_{e-e^-} + T_N + V_{NN}$$

with

$$T_e^- = \sum_{i=1}^{N} \left[ \frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{k^2}{2m_e} \right] \psi_i^2$$

$$V_{e-N} = \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \frac{(2 \alpha \epsilon)(-e)}{|\mathbf{r}_i - \mathbf{R}_\alpha|}$$

Coulomb attraction

$$V_{e-e^-} = \frac{1}{2} \sum_{i \neq j=1}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

electron-electron Coulomb repulsion

$$T_N = \sum_{\alpha=1}^{M} -\frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2$$

kin. energy of nuclei/ions

$$V_{NN} = \frac{1}{2} \sum_{\alpha_1 \beta=1}^{M} \frac{(2 \alpha_1 \epsilon)(2 \beta \epsilon)}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}$$

nucleus-nucleus (ion-ion) Coulomb repulsion

The time-dep. Schrödinger eq. has the form

$$\left[ H_{\text{cond. matter}}(x_i, \mathbf{\hat{R}}_\alpha) - \lambda (i) \frac{\partial}{\partial \epsilon} \right] \psi(x_i, \mathbf{\hat{R}}_\alpha; t) = 0$$

electrons nuclei/ions

with \( x_i = (\mathbf{r}_i, s_x^{(i)}) \) for electrons.
This problem is infinitely more complex than the atomic problem discussed earlier, because we now have two types of degrees of freedom: \( x_i \) for the electrons and \( \tilde{R}_j \) for the ions, and in general, their motion is coupled.

Useful approximation: "Born-Oppenheimer" (adiabatic)

\[ M_e \gg m_e \quad \text{nuclei ions move much slower than electrons} \]

\[ v_e = v_f = 10^8 \frac{\text{cm}}{\text{s}} \quad v_N = 10^5 \frac{\text{cm}}{\text{s}} \]

Hence, one may approximate \( T_N \approx 0 \) as far as electronic motion is concerned. One solves for the electronic problem with fixed ions of the nuclei ions:

\[
\begin{align*}
\hat{H}_{e} &= \left\{ \hat{p}_{e} \right\}^2 + \left\{ \hat{x}_{e} \right\}^2 + V_{e-N}(x_e) + V_{e-e}(x_e, x_i) \\
&= \text{fixed ions} + V_{NN}(\tilde{R}_i, \tilde{R}_j)
\end{align*}
\]

and the stationary Schrödinger eq. for the electrons becomes

\[
\begin{align*}
\hat{H}_{e} \psi_{e-N}(x_e) &= E \psi_{e-N}(x_e) \\
\end{align*}
\]

where the total energies and WFs for the quantum states depend parametrically on the positions \( \tilde{R}_i \) of the nuclei ions.
Boundary conditions

- atoms, molecules, clusters:
  - Wave functions vanish at \( r \rightarrow \infty \) (\( r \approx \text{large } r \), in practice)

- lattices (periodic structure)

  ![Diagram of a lattice structure]

  One idealizes the system by assuming a repetition of "unit cells" which are the basic building blocks. Each cell contains \( \approx 10^2 \) electrons.

  \[ \Rightarrow \text{impose periodic B.C.'s: } \psi_e(\vec{r}) = \psi_e(\vec{r} + \vec{a}) \]

  Constant displacement

Example 3: Structure of atomic nucleus

We model the nucleus as 2 types of interacting point particles (protons and neutrons) which can be distinguished by their isospin quantum number \( t_z \)

\[ t = \frac{1}{2} \left\{ \begin{array}{ll} t_z = +\frac{1}{2} & \text{protons} \\ t_z = -\frac{1}{2} & \text{neutrons} \end{array} \right. \]

The masses of protons and neutrons are almost the same, therefore one typically uses

\[ m = m_{\text{nucleon}} \approx 939 \text{ MeV}/c^2. \]
Nuclear Hamiltonian:

\[ H_{\text{nucleus}} = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^{N} V^{(2)}(x_i, x_j) \right) \]

\[ + \frac{1}{6} \sum_{i,j,k=1}^{N} V^{(3)}(x_i, x_j, x_k) \]

The degree of freedom in this case are:

\[ (x_i) = (\tilde{r}_i, s_z^{(i)} = \uparrow, t_z^{(i)} = p/h) \]

\textit{position spin isospin}

The 2-body interaction potential contains, of course, the Coulomb repulsion between the protons

\[ V^{(2)}_{\text{Coul}} = \frac{1}{2} \sum_{i,j=1}^{N} \frac{e^2}{|\tilde{r}_i - \tilde{r}_j|} \]

\textit{only protons}

But there is also an attractive term due to strong interaction

\[ V^{(2)}_{\text{strong}} = \frac{1}{2} \sum_{i,j=1}^{N} V^{(2)}(\tilde{r}_i, s_z^{(i)}, t_z^{(i)}, \tilde{r}_j, s_z^{(j)}, t_z^{(j)}) \]

which contains large \textit{spin-dependent terms} \((\tilde{r}_i \cdot \tilde{s}_i)\) and \((\tilde{s}_i \cdot \tilde{s}_j)\)

\textit{strong spin-orbit and strong spin-spin}

which cannot be treated by perturbation theory.

In nuclear case, one also has to add a 3-body interaction term \(V^{(3)}\) which has its origin in
multiple meson-exchanges (e.g. pion-pion,...). The structure of this term can be derived, in the static limit, from meson-nucleon quantum field theory.

Example 4: Interior of a star (astrophysics)

In general, very complicated: one has electrons, protons and neutrons, plus nuclei (e.g. 4He, 16O,...), all of which have kinetic energies plus corresponding interaction potentials. In special cases (neutron star) the density is so large that even the quark-substructure may play a role.

Possible simplifications: free electron gas, hydrodynamic description of interacting system using an empirical "equation of state".