Physics 8164 : Quantum theory of many-particle systems

1. Introduction

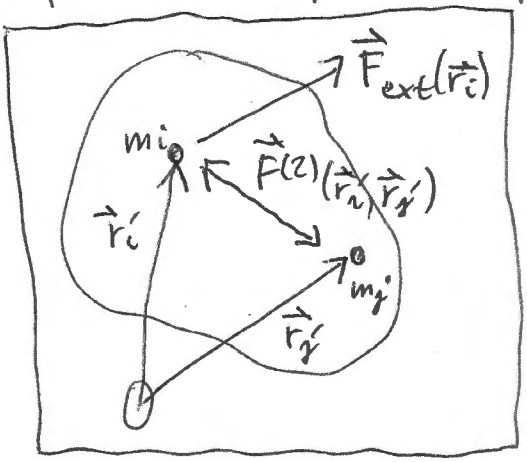
Textbook (Fetter & Walecka, p. 3): "The physical world consists of interacting many-particle systems"

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

- atoms ($Z \lesssim 120$)
- molecules / quantum chemistry ($N \approx 10 - 10^5$)
- condensed matter ($N \approx 10^{23}/cm^3$ in bulk material; $\sim 10^2$ electrons per "unit cell" of periodic lattice)
- atomic nuclei ($N \lesssim 300$)
- neutron stars ($\rho_0 \approx 0.14\, fm^{-3} \rightarrow N \approx 10^{38}/cm^3$)

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, chapter 1). We assume the particles interact via 2-body forces



$$\vec{F}^{(2)}(\vec{r}_i, \vec{r}_j) \longleftrightarrow V^{(2)}(\vec{r}_i, \vec{r}_j)$$

2-body force 2-body interaction

In addition, the system may experience an external force field

$$\vec{F}_{ext}(\vec{r}_i) \longleftrightarrow V_{ext}(\vec{r}_i)$$

Assuming conservative forces, one finds that the total energy E of this system is a constant of motion:

$$E = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m_i} + \sum_{i=1}^{N} V_{ext}(\vec{r}_i) + \frac{1}{2}\sum_{i,j=1\,(i\neq j)}^{N} V^{(2)}(\vec{r}_i, \vec{r}_j)$$

kinetic energy; external potential; 2-body interaction

The quantization of this expression is straightforward. In coordinate space, we have

classical	quantum
$\vec{r}_i$	$\hat{\vec{r}}_i \equiv \vec{r}_i$
$\vec{p}_i$	$\hat{\vec{p}}_i = -i\hbar\nabla_i$

and we put $E = H =$ Hamilton function $\rightarrow$ quantum Hamiltonian $\hat{H}$:

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{\hbar^2\nabla_i^2}{2m_i} + V_{ext}(\vec{r}_i)\right] + \frac{1}{2}\sum_{i,j=1\,(i\neq j)}^{N} V^{(2)}(\vec{r}_i, \vec{r}_j)$$

kinetic energy; external potential; 2-body interaction

Let us now consider a specific example, the N-electron atom.

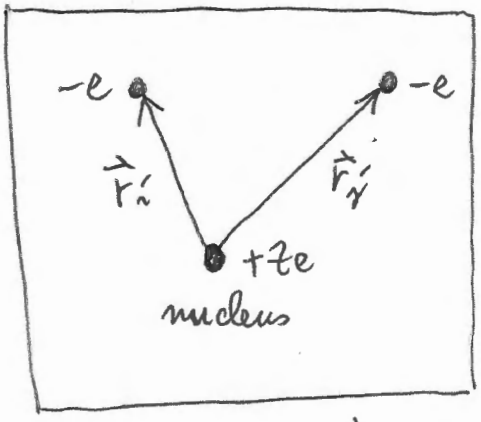
Example 1: N-electron atom

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 electrons is of order $r_e \approx \text{Å} = 10^{-10} m$. The atomic Hamiltonian has the structure (we use Coulomb potential in Gaussian units):

$$H_{atom} = H^0 + H'$$

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

- kinetic energy of electrons
- electron-nucleus Coulomb 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'). 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):

$$H'(\text{spin-orbit}) = \sum_{i=1}^{N} f(r_i)\, \vec{l}_i^{(e)} \cdot \vec{s}_i^{(e)}$$

where $\vec{l}_i^{(e)}$ is the orbital angular momentum operator for electron (i):

$$\vec{l}_i^{(e)} = \vec{r}_i \times (-i\hbar \nabla_i)$$

and $\vec{s}_i^{(e)}$ is the spin-operator for electron (i), given in terms of Pauli matrices $\vec{\sigma}_i^{(e)}$:

$$\vec{s}_i^{(e)} = \frac{\hbar}{2} \vec{\sigma}_i^{(e)}$$

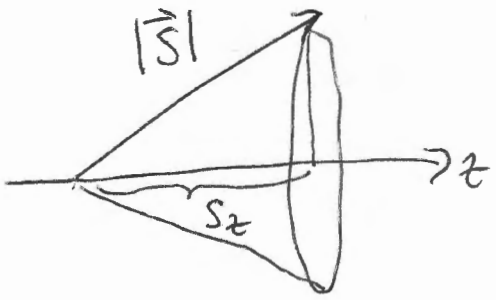
This spin-orbit term gives rise to the "fine-structure" splitting in atoms.

Taking spin into account, the atomic degrees of freedom are

$$(x_i) \equiv \left(\vec{r}_i \,,\ \underbrace{s_i = \tfrac{1}{2},\ s_{z(i)} = \pm \tfrac{\hbar}{2}}\right)$$

(x_i): all coordinates of electrons; $\vec{r}_i$: position; $s_i = \frac{1}{2}, s_{z(i)} = \pm \frac{\hbar}{2}$: spin; $i = 1, \ldots, N$

Significance of spin quantum number of electron:



$$|\vec{S}| = \hbar \sqrt{s(s+1)} \quad , s = \tfrac{1}{2}$$

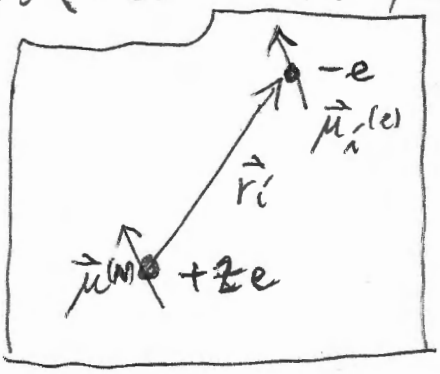
$$\Rightarrow |\vec{S}| = \hbar \sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right)} = \hbar \sqrt{\tfrac{3}{4}}$$

$$\underline{|\vec{S}| = \frac{\hbar}{2}\sqrt{3}}$$

and $\underline{S_z = \pm \frac{\hbar}{2}}$

Another spin-dep. term in H' is the interaction between

the electron magnetic moment $\vec{\mu}_i^{(e)}$ and the nuclear magnetic moment $\vec{\mu}^{(N)}$ which in many cases is non-zero (for "odd-even" nuclei); this interaction is tiny and gives rise to the "hyperfine" splitting of atomic levels (see Shankar, QM, chapter 15, p. 407)



$$H'(\text{hyperfine}) \propto \sum_{i=1}^{N} \vec{\mu}^{(N)} \cdot \vec{\mu}_i^{(e)}$$

$$\propto \sum_{i=1}^{N} \vec{S}^{(N)} \cdot \vec{S}_i^{(e)}$$

$\vec{S}^{(N)}$: nuclear spin; $\vec{S}_i^{(e)}$: electron spin

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So when we look at the structure of the atomic Hamiltonian we see that there are 2 basic types of operators!

$$\sum_{i=1}^{N} A(x_i) \hat{=} \text{one-body operator} = A^{(1)}$$

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

$$\frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^{N} B(x_i, x_j) = \text{two-body operator} = B^{(2)}$$

example: electron-electron Coulomb repulsion

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

One postulates that the Schrödinger eq. has the structure

$$\left[H_{atom}(x_1, x_2, \ldots, x_N) - i\hbar\frac{\partial}{\partial t}\right]\psi(x_1, x_2, \ldots, x_N; t) = 0$$

or in detail

$$\left.\begin{aligned}\Bigg[\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze^2}{|\vec{r}_i|}\right) + \frac{1}{2}\sum_{\substack{i,j=1\\(i\neq j)}}^{N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} \\ + H'(\text{spin-orbit}) + H'(\text{hyperfine}) + \ldots - i\hbar\frac{\partial}{\partial t}\Bigg] \\ \psi\left(\vec{r}_1, s_z^{(1)}; \vec{r}_2, s_z^{(2)}; \ldots; \vec{r}_N, s_z^{(N)}; t\right) = 0\end{aligned}\right\}$$

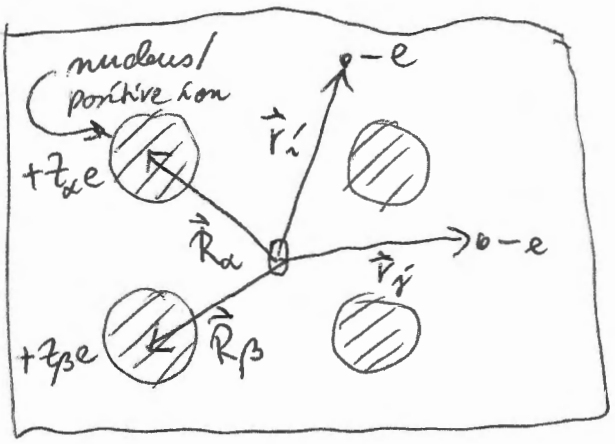
Now we can easily see why the solution of the N-body quantum problem is difficult! The N-body time-dep. Schrödinger eq. is a time-dep. partial differential eq. which

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

$\Rightarrow$ 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

$$T_{e^-} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla_i^2 \qquad \text{electron kin. energy}$$

$$V_{e^-,N} = \sum_{i=1}^{N}\sum_{\alpha=1}^{M} \frac{(Z_\alpha e)(-e)}{|\vec{r}_i - \vec{R}_\alpha|} \qquad \text{electron-nucleus(ion) Coulomb attraction}$$

$$V_{e^-e^-} = \frac{1}{2}\sum_{\substack{i,j=1 \\ (i\neq j)}}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \qquad \text{electron-electron Coulomb repulsion}$$

$$T_N = \sum_{\alpha=1}^{M} -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 \qquad \text{kin. energy of nuclei/ions}$$

$$V_{NN} = \frac{1}{2}\sum_{\substack{\alpha,\beta=1 \\ (\alpha\neq\beta)}}^{M} \frac{(Z_\alpha e)(Z_\beta e)}{|\vec{R}_\alpha - \vec{R}_\beta|} \qquad \text{nucleus-nucleus (ion-ion) Coulomb repulsion}$$

The time-dep. Schrödinger eq. has the form

$$\left[H_{\text{cond. matt}}\left(x_i, \vec{R}_\alpha\right) - i\hbar\frac{\partial}{\partial t}\right]\Psi(x_i, \vec{R}_\alpha; t) = 0$$

(x_i: electrons; $\vec{R}_\alpha$: nuclei/ions)

with $x_i \equiv (\vec{r}_i, s_z^{(i)})$ for electrons.

This problem is infinitely more complex than the atomic problem discussed earlier, because we now have 2 types of degrees of freedom: x_i for the electrons and $\vec{R}_\alpha$ for the ions, and in general, their motion is coupled.

Useful approximation: "Born-Oppenheimer" (adiabatic)

$M_\alpha >> m_e$ ⇒ nuclei/ions move much slower than electrons

$v_{e^-} \approx v_F = 10^8 \frac{cm}{s}$, $v_N \approx 10^5 \frac{cm}{s}$

Hence, one may approximate $\boxed{T_N \approx 0}$, as far as electronic motion is concerned. One solves for electronic problem for fixed positions of the nuclei/ions:

$$H_{e^-}^{\{\vec{R}_\alpha\}}(x_i) = T_{e^-} + V_{e^-,N}^{\{\vec{R}_\alpha\}}(x_i) + V_{e^-e^-}^{(2)}(x_i, x_j) + \underbrace{V_{NN}(\vec{R}_\alpha, \vec{R}_\beta)}_{= \text{const. Coul.}}$$

($\{\vec{R}_\alpha\}$: fixed ions)

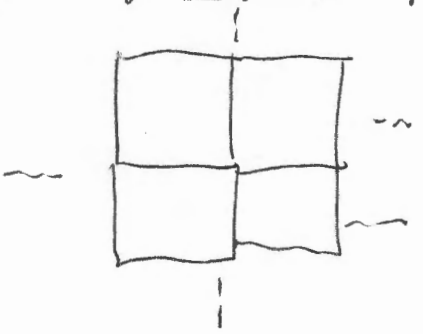
and the stationary Schrödinger eq. for the electrons becomes

$$\boxed{H_{e^-}^{\{\vec{R}_\alpha\}}(x_i)\, \psi_{e^-,\underline{n}}^{\{\vec{R}_\alpha\}}(x_i) = E_{e^-,\underline{n}}^{\{\vec{R}_\alpha\}}\, \psi_{e^-,\underline{n}}^{\{\vec{R}_\alpha\}}(x_i)}$$

where the total energies and WF's for the quantum states $\underline{n}$ depend parametrically on the positions $\vec{R}_\alpha$ of the nuclei/ions.

Boundary conditions

- atoms, molecules, clusters:
  → WF's vanish at $r \to \infty$ ($\approx$ large r, in practice)
- crystals (periodic structures)



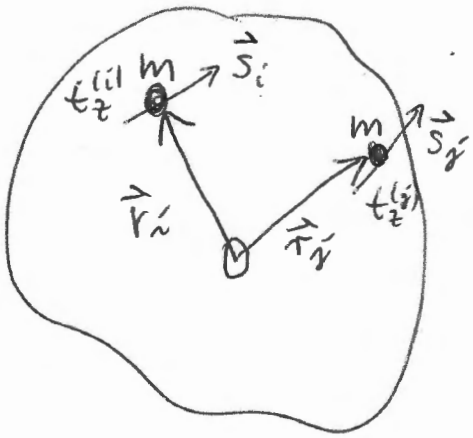
one idealizes the system by assuming a repetition of "unit cells" which are the basic building blocks. Each cell contains $\sim 10^2$ electrons.

→ impose periodic B.C.'s: $\Psi_{e^-}(\vec{r}_i) = \Psi_{e^-}(\vec{r}_i + \vec{a})$

($\vec{a}$: 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



$$t = \frac{1}{2} \begin{cases} t_z = +\frac{1}{2} & \text{protons} \\ t_z = -\frac{1}{2} & \text{neutrons} \end{cases}$$

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

$$m \equiv m_{nucleon} \approx 939\ \mathrm{MeV}/c^2.$$

Nuclear Hamiltonian:

$$H_{nucleus} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{2}\sum_{\substack{i,j=1 \\ (i\neq j)}}^{N} V^{(2)}(x_i, x_j) + \frac{1}{6}\sum_{i,j,k=1}^{N} V^{(3)}(x_i, x_j, x_k)$$

The degrees of freedom in this case are:

$$(x_i) = \underbrace{(\vec{r}_i}_{\text{position}}, \underbrace{s_z^{(i)} = \uparrow\downarrow}_{\text{spin}}, \underbrace{t_z^{(i)} = p/n}_{\text{isospin}})$$

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

$$V_{coul}^{(2)} = \frac{1}{2}\sum_{\substack{i,j=1 \\ \text{(protons only)}}}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

but there is also an attractive term due to strong interaction

$$V_{strong}^{(2)} = \frac{1}{2}\sum_{\substack{i,j=1 \\ (i\neq j)}}^{N} V^{(2)}(\vec{r}_i, s_z^{(i)}, t_z^{(i)}; \vec{r}_j, s_z^{(j)}, t_z^{(j)})$$

which contains large spin-dependent terms

$$\underbrace{(\vec{l}_i \cdot \vec{s}_i)}_{\text{strong spin-orbit}} \quad \text{and} \quad \underbrace{(\vec{s}_i \cdot \vec{s}_j)}_{\text{strong spin-spin}}$$

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, ^{16}O, ...), all of which have kinetic energies plus corresponding interaction potentials. In special cases (neutron star) the density is so large that even the quarks-substructure may play a role.

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