Chapter 6  Systems of Particles

Generalized Eigenvalue Equation

We write the multiparticle Hamiltonian $H$ which operates on a multiparticle wave state $\Psi$ yielding the total energy $E$ of the system.

$$H(1,2,3,4,5,...N) \Psi_n(1,2,3,4,...N) = E \Psi_n(1,2,3,4,...N)$$

This equation can only be solved on computers if at all for multiparticle states, molecules, etc.

Independent or Weakly interacting Particles

If the particles are weakly interacting we might consider the Hamiltonian as a sum of single particle Hamiltonians where the potential is a mean field felt by all particles equally.

$$(H(1)+H(2)+H(3)+...+H(N))\Psi_n(1,2,3,...N) = (E_{n1}+E_{n2}+E_{n3}+.....+E_{nN})\Psi_n(1,2,3,...N)$$

Perfectly Separable equation so choose a combination wave function

$$\Psi_{n1n2n3n4...nN} = \psi_{n1}(1) \psi_{n2}(2) \psi_{n3}(3) \psi_{n4}(4)...\psi_{nN}(N)$$

where we solve the system of single particle equations

$$H_{1}\psi_{n1}(1) = E_{n1}\psi_{n1}(1)$$
$$H_{2}\psi_{n2}(2) = E_{n2}\psi_{n2}(2)$$
$$H_{N}\psi_{nN}(N) = E_{nN}\psi_{nN}(N)$$

In principle we can solve one equation and have all the solutions.

Example:

Let a system of 4 particles be confined to an infinite square well of width $a$.

$$\psi_n(i) = \frac{2}{\sqrt{a}} \sin\left(\frac{n\pi x}{a}\right)$$
$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2$$

**ground state**

$$\Psi(1,2,3,4)_{n1n2n3n4} = \psi_{n1}(1)\psi_{n2}(2)\psi_{n3}(3)\psi_{n4}(4) \quad E = 4E_1$$
Distinguishable Particles

Classically we are able to label each particle and then in principle follow there time development. The wave function is just a product as we have seen.

\[ \Psi(1,2,3,4,\ldots,N) = \psi_a(1) \psi_b(2) \psi_c(3) \psi_d(4) \ldots \psi_N(N) \]

\[ \int |\Psi|^2 \, dV_{1,2,3,\ldots,N} = 1 \]

\[ = \left( \int |\psi_a(1)|^2 \, d^3x_1 \right) \left( \int |\psi_b(2)|^2 \, d^3x_2 \right) \left( \int |\psi_c(3)|^2 \, d^3x_3 \right) \ldots \left( \int |\psi_N(N)|^2 \, d^3x_N \right) \]

6-5 Indistinguishable Particles and Exchange Symmetry

Quantum mechanically we are not able to distinguish electrons, protons, neutrons, etc. from each other. They are classified as identical particles and exhibit exchange symmetry. Consider an operator which exchanges positions of particle \( I \) and \( J \), \( P_{Ij} \).

\[ P_{Ij} \Psi(1,2,3,\ldots,J,\ldots,N) = \Psi(1,2,3,J,\ldots,I,\ldots,N) \quad \text{define exchange operator } P \text{ exchanges particles } I \text{ and } J \]

\[ P_{Ij} \Psi(1,2,3,\ldots,J,\ldots,N) = \lambda \Psi(1,2,3,\ldots,J,\ldots,N) \quad \text{eigenvalue equation for } P_{Ij} \]

\[ P_{Ij} \Psi(1,2,3,\ldots,J,\ldots,N) = \lambda P_{Ij} \Psi(1,2,3,\ldots,J,\ldots,N) \quad \text{operate on left side again with } P_{Ij} \]

\[ \Psi(1,2,3,\ldots,J,\ldots,N) = \lambda \lambda \Psi(1,2,3,\ldots,J,\ldots,N) \quad \rightarrow \lambda^2 = 1 \]

\[ \lambda = +1 \quad \text{symmetric state} \quad \text{bosons} \quad \gamma, \alpha, \ldots \quad \text{integral spin} \]

\[ \lambda = -1 \quad \text{anti-symmetric state} \quad \text{fermions} \quad e, p, n, \ldots \quad \text{1/2 integral spin} \]

If the Hamiltonian of the system exhibits exchange symmetry then the wave function solutions must have either even or odd parity with respect to \( P_{Ij} \) exchange.

\[ \text{Example:} \]

Consider that \( [H(1,2,N), P_{Ij}] = 0 \)

\[ \text{eg, } H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_1 - r_2|} \]

Then \( H \) and \( P_{Ij} \) share the same wavefunctions

\[ H \Psi^\pm = E \Psi^\pm \quad \text{symmetric and antisymmetric wavefunctions} \]
Distinguishable Particles

\[ \Psi(1,2,3,4,...,N) = \psi_a(1) \psi_b(2) \psi_c(3) \psi_d(4) ... \psi_N(4) \]

Indistinguishable Particles (Symmetric and Anti-symmetric states)

For indistinguishable quantum particles the wave function must contain all combinatoric arrangements of particle lable \(1,2,3,...,N\) and quantum state \(a,b,c,...z\)

\[ \Psi_{a,b,c,...z}^{\pm}(1,2,3,...,N) = \frac{1}{\sqrt{n!}} \left\{ \psi_a(1) \psi_b(2) \psi_c(3) ... \psi_N(N) \pm \psi_a(1) \psi_b(2) \psi_c(3) ... \psi_N(N) \right\} \]

Slater Determinant Method

**Symmetric (all permutations + sign)**

\[ \Psi_{a,b}^{s}(1,2) = \begin{vmatrix} \psi_a(1) & \psi_a(2) \\ \psi_b(1) & \psi_b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\psi_a(1) \psi_b(2) + \psi_b(1) \psi_a(2)) \]

\[ \Psi_{a,b,c}^{s}(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \psi_a(3) \\ \psi_b(1) & \psi_b(2) & \psi_b(3) \\ \psi_c(1) & \psi_c(2) & \psi_c(3) \end{vmatrix} = \frac{1}{\sqrt{6}} \left( +\psi_a(1) \psi_b(2) \psi_c(3) + \psi_c(1) \psi_a(2) \psi_b(3) + \psi_b(1) \psi_c(2) \psi_a(3) \right) \]

**Anti-symmetric (cyclic permutations + sign, anti-cyclic permutation - sign)**

\[ \Psi_{a,b}^{s}(1,2) = \begin{vmatrix} \psi_a(1) & \psi_a(2) \\ \psi_b(1) & \psi_b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\psi_a(1) \psi_b(2) - \psi_b(1) \psi_a(2)) \]

\[ \Psi_{a,b,c}^{s}(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \psi_a(3) \\ \psi_b(1) & \psi_b(2) & \psi_b(3) \\ \psi_c(1) & \psi_c(2) & \psi_c(3) \end{vmatrix} = \frac{1}{\sqrt{6}} \left( +\psi_a(1) \psi_b(2) \psi_c(3) + \psi_c(1) \psi_a(2) \psi_b(3) + \psi_b(1) \psi_c(2) \psi_a(3) \right) \]

Notice that when \(a=b\) the fermion wavefunction vanishes (two rows in the determinant are the same!)  
*This leads to the Pauli Exclusion Principle - No two fermions can be in the same quantum state!*
Exchange Force

Classical

\[ < \Psi_{1,2}^{\text{classical}} | (x_1 - x_2)^2 | \Psi_{1,2}^{\text{classical}} > = < \Psi_{1a} | \psi_{2b} \| (x_1 - x_2)^2 | \Psi_{1a} > \psi_{2b} > \\
= < \Psi_{1a} | x_1^2 | \Psi_{1a} > < \Psi_{2b} | \psi_{2b} > + < \Psi_{1a} | \psi_{1a} > < \Psi_{2b} | x_2^2 | \psi_{2b} > - 2 < \Psi_{1a} | x_1 | \Psi_{1a} \times < \Psi_{2b} | x_2 | \psi_{2b} > \\
< (x_1 - x_2)^2 > = < x^2 >_a + < x^2 >_b - 2 < x >_a < x >_b = \Delta \\

Boson and Fermions \ a \neq b

\[ < \Psi_{1,2}^{\pm} | (x_1 - x_2)^2 | \Psi_{1,2}^{\pm} > = \frac{1}{2} \left( < \Psi_{1a} | \psi_{2b} | \pm < \Psi_{1b} | \psi_{2a} > \right) (x_1 - x_2)^2 (| \Psi_{1a} > \psi_{2b} > \pm | \Psi_{1b} > \psi_{2a} > ) \\
= \frac{1}{2} < \Psi_{1a} | \psi_{2b} | (x_1 - x_2)^2 (| \Psi_{1a} > \psi_{2b} > ) \\
+ \frac{1}{2} < \Psi_{1b} | \psi_{2a} | (x_1 - x_2)^2 (| \Psi_{1b} > \psi_{2a} > ) \\
\pm \frac{1}{2} < \Psi_{1a} | \psi_{2b} | (x_1 - x_2)^2 (| \Psi_{1b} > \psi_{2a} > ) \\
\pm \frac{1}{2} < \Psi_{1b} | \psi_{2a} | (x_1 - x_2)^2 (| \Psi_{1b} > \psi_{2a} > ) \\
= \Delta \pm \left( \frac{1}{2} < \Psi_{1b} | x_1^2 | \Psi_{1a} > < \psi_{2a} | \psi_{2b} > \pm \frac{1}{2} < \Psi_{1b} | \Psi_{1a} \times \psi_{2a} | x_2^2 | \psi_{2b} > \mp < \Psi_{1b} | x_1 | \Psi_{1a} \times < \Psi_{2a} | x_2 | \psi_{2b} > \right) \times \frac{2}{\Delta} \\
= \Delta \pm \left( \frac{1}{2} < \Psi_{1b} | x_1^2 | \Psi_{1a} > \delta_{ab} \pm \frac{1}{2} \delta_{ab} < \psi_{2a} | \psi_{2b} > \delta_{ab} \mp < \Psi_{1b} | x_1 | \Psi_{1a} \times < \Psi_{2a} | x_2 | \psi_{2b} > \right) \times \frac{2}{\Delta} \\
< (x_1 - x_2)^2 > = \Delta \mp < \psi_a | x | \psi_a >^2 = \Delta \mp < x >_a^2 \\

We see that identical bosons have an affinity to be closer than than \Delta and fermions have an affinity to be spaced apart further than \Delta. This gives rise to the concept of an exchange force attracting bosons and repelling fermions.

The overlap integral \( < x >_a = \int \psi_a^* x \psi_a dx \) defines the deviation from classical behavior. If the particles are far apart then \( < x >_a = 0 \) and the system approaches classical behavior.
6–4 Two Particle Hamiltonian

The system of particles can be viewed as motion of the center of mass frame \( X \), and motion within a relative coordinate system \( x \).

\[
H(1,2) = \frac{\hbar^2}{2m_1} \frac{d^2}{dx_1^2} + \frac{\hbar^2}{2m_2} \frac{d^2}{dx_2^2} + V(|x_1 - x_2|)
\]

Two particle hamiltonian

\[
X = \frac{m_1x_1 + m_2x_2}{m_1 + m_2}
\]

CM coordinate

\[
x = x_1 - x_2
\]

relative coordinate

CM system

\[
\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1} + \frac{1}{m_1} \frac{\partial}{\partial x_1} \quad \frac{\partial}{\partial x_2} = \frac{\partial X}{\partial x_2} + \frac{1}{m_2} \frac{\partial}{\partial x_2}
\]

Doppler Broadening

Consider a atomic gas at temperature \( T \). You measure the transition energies in a spectroscope. The perfectly sharp atomic transition lines are Doppler broadened by the motion of the atoms or molecules under study.

\[
<E> = \left< E_{\text{CM}} \right> + \left< E_{\text{atomic}} \right>
\]