

Many-particle systems

Quantum Chemistry

Lesson 4

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State (of a many-particle system)

Wave function (X-representation)

- spin-less particles
 - $\varphi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$
 - $\int_{\mathbb{R}^{3N}} |\varphi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d^3\vec{r}_1 d^3\vec{r}_2 \dots d^3\vec{r}_N < +\infty$ [$\varphi \in L_2(\mathbb{R}^{3N})$]
 - interpretation of $|\varphi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2$ and $\int_{V_1 \times V_2 \times \dots \times V_N} |\varphi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d^3\vec{r}_1 d^3\vec{r}_2 \dots d^3\vec{r}_N$ for normalized functions ($\int_{\mathbb{R}^{3N}} |\varphi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d^3\vec{r}_1 d^3\vec{r}_2 \dots d^3\vec{r}_N = 1$)
- particles with non-zero spin
 - $\varphi(\vec{r}_1, \xi_1; \vec{r}_2, \xi_2; \dots, \vec{r}_N, \xi_N)$
 - $\forall \xi_1, \xi_2, \dots, \xi_N: \int_{\mathbb{R}^{3N}} |\varphi(\vec{r}_1, \xi_1; \vec{r}_2, \xi_2; \dots, \vec{r}_N, \xi_N)|^2 d^3\vec{r}_1 d^3\vec{r}_2 \dots d^3\vec{r}_N < +\infty$
 - interpretation of $|\varphi(\vec{r}_1, \xi_1; \vec{r}_2, \xi_2; \dots, \vec{r}_N, \xi_N)|^2$ and $\int_{\mathbb{R}^{3N}} |\varphi(\vec{r}_1, \xi_1; \vec{r}_2, \xi_2; \dots, \vec{r}_N, \xi_N)|^2 d^3\vec{r}_1 d^3\vec{r}_2 \dots d^3\vec{r}_N$ for normalized functions ($\sum_{\xi_1, \xi_2, \dots, \xi_N} \int_{\mathbb{R}^{3N}} |\varphi(\vec{r}_1, \xi_1; \vec{r}_2, \xi_2; \dots, \vec{r}_N, \xi_N)|^2 d^3\vec{r}_1 d^3\vec{r}_2 \dots d^3\vec{r}_N = 1$)
- reduced notation
 - $\varphi(1, 2, \dots, N)$, where 1 stands for \vec{r}_1, ξ_1 (or \vec{r}_1 if the spin is neglected) etc.,
 - $\int |\varphi(1, 2, \dots, N)|^2 d1 d2 \dots dN$, where $\int \dots d1 = \sum_{\xi_1} \int \dots d^3\vec{r}_1$ (or $\int \dots d^3\vec{r}_1$) etc.

Observables, operators, Schrödinger equation

Position and linear momentum (X-representation)

- $\hat{X}_K = [x_K, y_K, z_K] = \vec{r}_K$
- $\hat{P}_K = \left[-i\hbar \frac{\partial}{\partial x_K}, -i\hbar \frac{\partial}{\partial y_K}, -i\hbar \frac{\partial}{\partial z_K} \right] = -i\hbar \nabla_K$

Energy, Hamiltonian

- $H(\vec{p}_1, \vec{r}_1; \vec{p}_2, \vec{r}_2; \dots; \vec{p}_N, \vec{r}_N) = \sum_{K=1}^N \frac{\vec{p}_K^2}{2m_K} + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$
- $\hat{H} = \sum_{K=1}^N \left(-\frac{\hbar^2}{2m_K} \Delta_K \right) + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) + \hat{V}$ (if spin-dependent interactions are considered, the spin-orbit interaction)

Observables, operators, Schrödinger equation

Stationary SE

- $\sum_{K=1}^N \left(-\frac{\hbar^2}{2m_K} \Delta_K \varphi \right) + V\varphi = E\varphi$

or (if spin-dependent interactions are to be considered)

$$\sum_{K=1}^N \left(-\frac{\hbar^2}{2m_K} \Delta_K \Phi \right) + \hat{V}\Phi = E\Phi$$

- $\int |\varphi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d^3\vec{r}_1 d^3\vec{r}_2 \dots d^3\vec{r}_N < +\infty$

or

$$\int_{\mathbb{R}^{3N}} \|\Phi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)\|^2 d^3\vec{r}_1 d^3\vec{r}_2 \dots d^3\vec{r}_N < +\infty$$

Observables, operators, Schrödinger equation

Non-interacting particles (ideal gas)

- $V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{K=1}^N V_K(\vec{r}_K)$

$$\hat{H} = \sum_{K=1}^N \left[-\frac{\hbar^2}{2m_K} \Delta_K + V_K(\vec{r}_K) \right] = \sum_{K=1}^N \hat{H}_K$$

$$\sum_{K=1}^N \hat{H}_K \varphi = E \varphi$$

- separation of particle variables:
 - $\varphi(1, 2, \dots, N) = \varphi_1(1) \varphi_2(2) \dots \varphi_N(N)$
 - $\hat{H}_K \varphi_K = E_K \varphi_K, \int \varphi_K dK < +\infty$
 - $\sum_{K=1}^N E_K = E$

Permutations

Permutation, transposition

- *permutation*: one-to-one mapping of an n -element set to itself, $\pi: \{1,2,3, \dots, N\} \rightarrow \{1,2,3, \dots, N\}$, reordering the set
- *transposition*: exchange of two elements, $\pi_{IJ}(I) = J, \pi_{IJ}(J) = I, \pi_{IJ}(K) = K$ pro $K \neq I, J$
- properties
 - permutations form a finite set (finite group, multiplication = composition) which contains $N!$ elements
 - every permutation can be composed of a finite series of transpositions, ...
 - the number of such transpositions is not unique, but it is either even or odd ...
 - one can thus distinguish between *even* and *odd* permutations, respectively (*permutation parity*)

Sign of permutation

- $\text{sgn}(\pi) = +1$ if π is even
- $\text{sgn}(\pi) = -1$ if π is odd

Identical particles

Identical particles

- particles which have the same “fundamental” properties (mass, charge, spin magnitude etc.)

Indistinguishability principle

- *classical physics*: identical particles can in principle be distinguished from one other (classical non-crossing trajectories)
- *quantum physics*: identical particles cannot be distinguished from one other (overlapping wave functions and/or density probabilities)
- an important consequence:
 - permutations of identical particles do not change the (quantum) state of the many-particle system
- an important question:
 - may the corresponding many-particle wave function change upon a permutation of particles?

Identical particles

Wave function for a system of identical (= indistinguishable) particles

- quantum state = a ray (1D subspace) in the Hilbert state space, $\{\alpha\varphi(1,2, \dots, N), \alpha \in \mathbb{C}\}$
- if a transposition, π_{IJ} , is applied
 - $\varphi(\pi_{IJ}[1,2, \dots, N]) = \alpha\varphi(1,2, \dots, N)$, α does not depend on I, J
 - $\varphi(\pi_{IJ}[\pi_{IJ}[1,2, \dots, N]]) = \begin{cases} \alpha\varphi(\pi_{IJ}[1,2, \dots, N]) = \alpha^2\varphi(1,2, \dots, N) \\ \varphi(1,2, \dots, N) \end{cases}$
 - $\alpha^2 = 1 \rightarrow \alpha = \pm 1$
- two kinds of wave function behavior
 - $\varphi(\pi[1,2, \dots, N]) = \varphi(1,2, \dots, N) \rightarrow$ **symmetric wave functions**
 - $\varphi(\pi[1,2, \dots, N]) = \text{sgn}(\pi)\varphi(1,2, \dots, N) \rightarrow$ **antisymmetric wave functions**

Identical particles

Fermions and bosons

- symmetry / antisymmetry of a wave function is not changed by either the time evolution or an (instantaneous) measurement
- two kinds of particles
 - **bosons**: symmetric wave functions (integer spin)
 - **fermions**: antisymmetric wave functions (half-integer spin)
- **electrons are fermions!**

Symmetric and antisymmetric subspaces of the Hilbert state space

- $\mathcal{H} \rightarrow \begin{cases} \mathcal{H}_S \\ \mathcal{H}_A \end{cases}, \quad \mathcal{H}_S \cap \mathcal{H}_A = \{|0\rangle\}, \quad \mathcal{H}_S \perp \mathcal{H}_A$
- *symmetrization operator*: $\varphi \in \mathcal{H} \Rightarrow \varphi_S = \hat{S}\varphi \equiv \frac{1}{N!} \sum_{\pi} \varphi(\pi[1,2, \dots, N]) \in \mathcal{H}_S \quad (\hat{S}^2 = \hat{S}, \hat{S}\mathcal{H} = \mathcal{H}_S)$
- *antisymmetrization operator*: $\varphi \in \mathcal{H} \Rightarrow \varphi_A = \hat{A}\varphi \equiv \frac{1}{N!} \sum_{\pi} \text{sgn}(\pi) \varphi(\pi[1,2, \dots, N]) \in \mathcal{H}_A \quad (\hat{A}^2 = \hat{A}, \hat{A}\mathcal{H} = \mathcal{H}_A)$

Identical particles

Non-interacting identical (= indistinguishable) particles

- Hamiltonian eigenfunctions:
 - $\varphi(1,2,, \dots, N) = \varphi_1(1)\varphi_2(2) \dots \varphi_N(N)$, $\langle \varphi_I | \varphi_J \rangle \equiv \int \varphi_I(x)^* \varphi_J(x) dx = \delta_{IJ}$... one-particle eigenfunctions
- normalized symmetric/antisymmetric wave functions
 - $\varphi_S \equiv \frac{1}{\sqrt{n_1!n_2!\dots}} \hat{S} \varphi = \frac{1}{\sqrt{N!n_1!n_2!\dots}} \sum_{\pi} \varphi_1(\pi[1])\varphi_2(\pi[2]) \dots \varphi_K(\pi[N])$, $K \leq N$
 - $\varphi_A \equiv \frac{1}{\sqrt{N!}} \hat{A} \varphi = \frac{1}{\sqrt{N!}} \sum_{\pi} \text{sign}(\pi) \varphi_1(\pi[1])\varphi_2(\pi[2]) \dots \varphi_N(\pi[N])$

Identical particles

Non-interacting identical (= indistinguishable) fermions – Slater determinant

- $\varphi(1, 2, \dots, N) = \varphi_1(1)\varphi_2(2) \dots \varphi_N(N)$
- $\varphi_A \equiv \sqrt{N!} \hat{A}\varphi = \frac{1}{\sqrt{N!}} \sum_{\pi} \text{sign}(\pi) \varphi_1(\pi[1])\varphi_2(\pi[2]) \dots \varphi_N(\pi[N]) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \varphi_1(1) & \dots & \varphi_N(1) \\ \vdots & \ddots & \vdots \\ \varphi_1(N) & \dots & \varphi_N(N) \end{pmatrix}$
- note that
 - φ_A is normalized (one-particle wave functions are orthonormal!)
 - such a wave function may accurately represent an energy (Hamiltonian) eigenfunction of a system of non-interacting particles
 - for interacting particles it holds only approximately (the *Hartree-Fock method*), ...
 - with the errors introduced being largely reduced if more than one (many) Slater determinants are used (*post Hartree-Fock methods*)

(Many-electron) atoms and molecules

Wave function

- $\varphi(\vec{R}_1, \Xi_1, \dots, \vec{R}_N, \Xi_N; \vec{r}_1, \xi_1, \dots, \vec{r}_n, \xi_n) \rightarrow \varphi(\vec{R}_K, \Xi_K; \vec{r}_k, \xi_k)$
 - \vec{R}_K, Ξ_K - atomic nuclei, \vec{r}_k, ξ_k - electrons
 - symmetry / antisymmetry to be applied for the nuclear degrees of freedom where needed
 - antisymmetry to be applied for the electronic degrees of freedom (always)

Hamilton operator (X-representation), electrostatic approximation

$$\hat{H} = \sum_{K=1}^N \left(-\frac{\hbar^2}{2M_K} \Delta_K \right) + \sum_{k=1}^n \left(-\frac{\hbar^2}{2m_e} \Delta_k \right) + \sum_{I < J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{R}_I - \vec{R}_J\|} + \sum_{i < j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_i - \vec{r}_j\|} - \sum_{I,i} \frac{Z_I e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{R}_I - \vec{r}_i\|}$$

The end of lesson 4.