
1 Hamiltonian in Magnetic Field

1.1 Hamiltonian Mechanics

1.2 Electromagnetic Field

1.3 Hamiltonian in Electromagnetic Field

Schrödinger Equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{1}{2m} (-i\hbar \nabla - z\mathbf{A}) \cdot (-i\hbar \nabla - z\mathbf{A}) \Psi + z\phi \Psi \quad (1)$$

which is linear on ϕ and quadratic on \mathbf{A} .

1.4 Spin

Revised one-electron Hamiltonian:

$$H = \frac{p^2}{2m_e} + \frac{e}{m_e} \mathbf{A} \cdot \mathbf{p} + \frac{e}{m_e} \mathbf{B} \cdot \mathbf{s} + \frac{e^2}{2m_e} A^2 + e\phi \quad (2)$$

where the:

- $\mathbf{A} \cdot \mathbf{p}$ term is the coupling of magnetic field with electron orbital motion
- $\mathbf{B} \cdot \mathbf{s}$ term is the coupling of magnetic field with spin
- A^2 term is the correction to the scalar potential ϕ

1.5 Molecular Electronic Hamiltonian

Molecular electronic Hamiltonian in atomic units:

$$H = \frac{1}{2} \sum_i p_i^2 - \sum_{K,i} \frac{Z_K}{r_{iK}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_{K>L} \frac{Z_K Z_L}{R_{KL}} \quad (3)$$
$$+ \sum_i \mathbf{A}_i(\mathbf{r}_i) \cdot \mathbf{p}_i + \sum_i \mathbf{B}(\mathbf{r}_i) \cdot \mathbf{s}_i - \sum_i \phi(\mathbf{r}_i) + \frac{1}{2} \sum_i A^2(\mathbf{r}_i)$$

In perturbative treatment we can write the Hamiltonian as:

$$H = H^{(0)} + H^{(1)} + H^{(2)} \quad (4)$$

where

$$H^{(1)} = \sum_i \mathbf{A}_i(\mathbf{r}_i) \cdot \mathbf{p}_i + \sum_i \mathbf{B}(\mathbf{r}_i) \cdot \mathbf{s}_i - \sum_i \phi(\mathbf{r}_i) \quad (5)$$

and the first two terms are the paramagnetic contribution to the Hamiltonian, and the diamagnetic contribution is:

$$H^{(2)} = \frac{1}{2} \sum_i A^2(\mathbf{r}_i) \quad (6)$$