

Quantum Description of the Nuclei-Electron System

Tutor: Edrick

Content

- Review: Time-Independent Schrödinger Equation
- Evolution Equation for Expansion Coefficients
- Coupled-Channel Equation

Time-Independent Schrödinger Equation ($\Psi \equiv \Psi(x, t)$)

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$

$$\Psi(x, t) = \psi(x) f(t)$$

$$\frac{\partial \Psi}{\partial t} = \psi \frac{df}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} f$$

$$i\hbar \psi \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} f + V\psi f.$$

$$i\hbar \frac{1}{f} \frac{df}{dt} = E$$

$$\downarrow \frac{df}{dt} = -\frac{iE}{\hbar} f,$$

$$i\hbar \frac{1}{f} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V$$

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V\psi = E\psi$$

$$f(t) = e^{-iEt/\hbar}$$

Goal

To study the evolution equation of the expansion coefficients, with respect to the adiabatic basis, of the wave function associated with the system electron-nuclei.

Evolution Equation for Coefficients

$$n \in \mathbb{Z}$$

$$H$$

$$|\varphi_n\rangle \longrightarrow H |\varphi_n\rangle = E_n |\varphi_n\rangle$$

$$|\psi(t)\rangle = \sum_n c_n(t) |\varphi_n\rangle$$

$$i\hbar \frac{d}{dt} \langle \varphi_n | \psi(t) \rangle = \langle \varphi_n | H | \psi(t) \rangle$$

$$i\hbar \frac{d}{dt} c_n(t) = E_n c_n(t)$$

$$\alpha \in \mathbb{R}$$

$$H$$

$$|w_\alpha\rangle \longrightarrow H |w_\alpha\rangle = E(\alpha) |w_\alpha\rangle$$

$$|\psi(t)\rangle = \int d\alpha c(\alpha, t) |w_\alpha\rangle$$

$$i\hbar \partial_t \langle w_\alpha | \psi(t) \rangle = \langle w_\alpha | \hat{H} | \psi(t) \rangle$$

$$i\hbar \partial_t c(\alpha, t) = E(\alpha) c(\alpha, t)$$

Coupled-Channel Equation: System

$$\mathcal{H} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0} \sum_{I < J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Coupled-Channel Equation

$$\left[- \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_I\}) \right] \chi_k + \sum_l C_{kl} \chi_l = i\hbar \frac{\partial}{\partial t} \chi_k$$

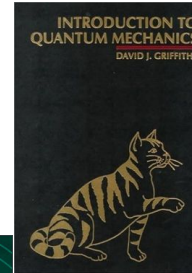
Coefficients

Sign inside parenthesis!

Couplings

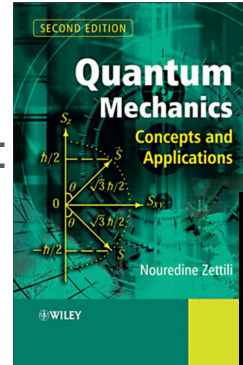
References

- Time-independent Schrödinger Equation :



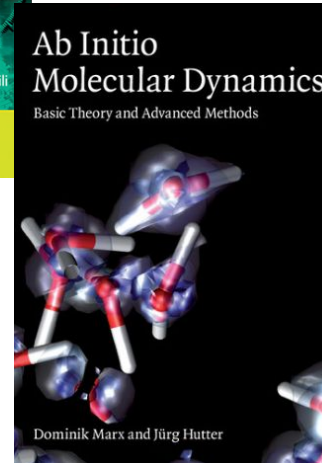
, Section 2.1

- Bounded & Unbounded States:



, Section 4.2

- Couple-Channel equation: Notes and



, First couple of pages in chapter 2 &

references therein