CH651 Assignment 2, Wednesday, October 22, 2014. Due Wednesday October 29, 2014

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Q1 In class we employed a small τ approximation to the operator $\exp[-\tau(\hat{\mathrm{A}}+\hat{\mathrm{B}})]$ where the operators $\hat{\mathrm{A}}$ and $\hat{\mathrm{B}}$ did not commute *i.e.* $[\hat{\mathrm{A}},\hat{\mathrm{B}}] \neq 0$. In particular we used the approximation $\exp[-\tau(\hat{\mathrm{A}}+\hat{\mathrm{B}})] = \exp[-\tau\hat{\mathrm{A}}]\exp[-\tau\hat{\mathrm{B}}] + \mathcal{O}(\tau^2)$, *i.e.* we used an approximation that was exact to first order in τ, so that the error was of order τ^2, *i.e.* $\mathcal{O}(\tau^2)$.

(i) Compute the error term that is $\mathcal{O}(\tau^2)$ with this approximation.

(ii) Suppose we were to use the following approximation:

$\exp[-\tau(\hat{\mathrm{A}}+\hat{\mathrm{B}})] \sim \exp[-\frac{\tau}{2}\hat{\mathrm{A}}]\exp[-\tau\hat{\mathrm{B}}]\exp[-\frac{\tau}{2}\hat{\mathrm{A}}]$.

Compute error term that is $\mathcal{O}(\tau^2)$ with this approximation. Comment on the accuracy of this approximate form.

Q2 Consider a time dependent hamiltonian in which the potential energy depends on time so $\hat{H}(t) = \hat{p}^2/2m + V(\hat{x}, t)$.

(i) For this hamiltonian, compute the commutator $[\hat{H}(t_1), \hat{H}(t_2)]$ for $t_1 \neq t_2$.

(ii) In class we realized that when the hamiltonian is time dependent the propagator for the time dependent Schrödinger equation should take the form $\exp[-(i/\hbar)\int_0^\infty \hat{H}(t)dt]$. Consider two times t_1 and t_2 that are infinitesimally displaced so $t_2 = t_1 + \tau$, where τ is the small positive displacement in time. Write down an approximation, accurate to first order in τ, to the propagator $K(x_2, t_2, x_1, t_1)$ that evolves the system from x_1 at t_1 to x_2 at t_2.

(iii) Show how you would use your approximate propagator from (ii) to evolve the wave function from its initial shape at t_1 to its final shape at t_2.

Q3 In class we made use of the complete orthogonal set of eigenfunctions of the momentum operator to transform between position and momentum representations. In the position representation, the momentum eigenstates have the following form: $\langle x|k\rangle = \frac{1}{\sqrt{2\pi}}\exp[ikx]$.

(i) Show that these functions are eigenfunctions of the momentum operator and give their eigenvalues. Show that these functions are also eigenfunctions of the free particle hamiltonian operator. Further, show that they CAN NOT be normalized in the usual sense. What does this tell you about a free particle of mass M with a definite energy $E = \hbar^2k^2/2M$.

(ii) Despite these problems of normalization, the momentum eigenfunctions are particularly useful for their mathematical properties. Linear combinations of these un-normalizable functions can actually be used to represent normalized wave packets. For example, let $C(k)$ be the coefficient function that gives the amplitude of each free particle energy or momentum eigenstate in an expansion of a wave packet of the following form:

$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} C(k) \exp[i(kx - \frac{\hbar k^2}{2M} t)] dk$

Suppose the coefficients of the different momentum eigenfunctions are given by

$C(k) = N \exp[-a(k-k_0)^2]$.

Using the following result: $I = \int_{-\infty}^{\infty} \exp[-\alpha x^2 + \beta x] dx = \sqrt{\pi/\alpha} \exp[\beta^2/4\alpha]$, obtain an expression for the resulting wave packet, $\psi(x,t)$.

(iii) Set $t = 0$ and show that the wave packet constructed in this way can be normalized

(iv) You should be able to rearrange your expression for the time dependent wave packet to show that it has the form of a real valued function multiplied by a phase factor. The real valued function will have the form of a traveling gaussian with time dependent mean position, $x_0(t)$, and variable width, $\sigma(t)$, *i.e.* the real valued part will have the form $\exp[-(x - x_0(t))^2/2\sigma^2(t)]$. Obtain simple expressions for $x_0(t)$ and $\sigma(t)$ and interpret your results.

Q4 Consider the time dependent Schrödinger equation for a system of electrons at positions x, and nuclei of mass M at positions R

$$i\hbar \frac{\partial \Psi(x,R,t)}{\partial t} = \hat{H} \Psi(x,R,t) \tag{1}$$

where the total Hamiltonian is written in the usual way, $\hat{H} = \frac{-\hbar^2}{2M} \nabla_R^2 + \hat{H}_{el}(x,R)$, in terms of the nuclear kinetic operator and the electronic Hamiltonian $\hat{H}_{el}$, which is an operator in the electronic sub-space that depends parametrically on the nuclear configuration. In the adiabatic representation, we write the coupled electron-nuclear wave function using the Born-Huang expansion

$$\Psi(x,R,t) = \sum_n \chi_n^a(R,t) \Phi_n^a(x,R) \tag{2}$$

in terms of the unique orthonormal, complete basis set, $\Phi_n^a(x,R)$, of instantaneous adiabatic electronic states defined as the set of eigenfunctions of the electronic Hamiltonian with eigenenergies $E_n(R)$ which depend on nuclear configuration. The adiabatic basis functions satisfy the eigenvalue problem $\hat{H}_{el}(R)\Phi_n^a(x,R) = E_n(R)\Phi_n^a(x,R)$ for each nuclear configuration, R. In class we showed that the time dependent expansion coefficient functions of this basis set, $\chi_n^a(R,t)$, satisfy the following equations of motion:

$$i\hbar \dot{\chi}_m^a = \frac{-\hbar^2}{2M} \nabla_R^2 \chi_m^a + E_m(R) \chi_m^a - \frac{\hbar^2}{2M} \sum_n \{ 2 \langle \Phi_m^a | \nabla_R | \Phi_n^a \rangle \cdot \nabla_R + \langle \Phi_m^a | \nabla_R^2 | \Phi_n^a \rangle \} \chi_n^a \tag{3}$$

and the brackets in the above result contain matrix elements that involve integrals over the electronic coordinates x only. In this representation all the coupling between coefficient functions of different electronic surfaces arises from the action of the nuclear kinetic operator on the adiabatic electronic basis states due to the parametric dependence of these basis states on nuclear configuration. These coupling terms appear in the last term on the right hand side of the above expression. If this term is small compared to the other terms in this equation and approximately set to zero, we see that the adiabatic coefficient functions, $\chi_m^a(R)$, for different electronic states evolve independently and we arrive at the Born-Oppenheimer approximation.

Consider a two electronic state, one nuclear degree of freedom system for which the electronic hamiltonian matrix elements in a so called diabatic representation are given by the following functions $\langle\Phi_1^d|\hat{H}_{el}|\Phi_1^d\rangle = \epsilon_1(R)$, $\langle\Phi_2^d|\hat{H}_{el}|\Phi_2^d\rangle = \epsilon_2(R)$ and $\langle\Phi_1^d|\hat{H}_{el}|\Phi_2^d\rangle = \langle\Phi_2^d|\hat{H}_{el}|\Phi_1^d\rangle = \Delta(R)$. Assume these diabatic basis functions form a complete orthonormal set.

(i) Give expressions for the adiabatic eigenstate energies $E_1(R)$, and $E_2(R)$, and show that the corresponding adiabatic eigenfunctions can be written as the following linear combinations of the diabatic functions:

$$\begin{aligned} \Phi_1^a(x,R) &= \cos[\theta(R)]\Phi_1^d(x) + \sin[\theta(R)]\Phi_2^d(x) \\ \Phi_2^a(x,R) &= -\sin[\theta(R)]\Phi_1^d(x) + \cos[\theta(R)]\Phi_2^d(x) \end{aligned} \tag{4}$$

Where $\theta(R)$ is the so called mixing angle of the transformation between the diabatic and adiabatic basis states and it depends on nuclear configuration according to the following:

$$\theta(R) = \frac{1}{2}(\pi/2 - \alpha(R)) \tag{5}$$

with

$$\alpha(R) = \sin^{-1}\left[\frac{(\epsilon_2(R) - \epsilon_1(R))}{\sqrt{(\epsilon_2(R) - \epsilon_1(R))^2 + 4\Delta^2(R)}}\right] \tag{6}$$

(ii) Use the above results to compute the derivative and second derivative nonadiabatic coupling matrices appearing in Eq.(3).

(iii) Compute the adiabatic Hellman-Feynman force matrix elements $\langle\Phi_m^a|\frac{\partial\hat{H}_{el}}{\partial R}|\Phi_n^a\rangle$ for our two state model.

Q5 (a) Solve Heisenberg's equations of motion

$$\frac{d\hat{A}_H}{dt} = \frac{i}{\hbar}[\hat{H}_H, A_H] \tag{7}$$

for the time evolution of the raising and lowering operators $\hat{A}_H = \hat{b}_H^+$ and $\hat{A}_H = \hat{b}_H$ for a harmonic oscillator where we can write the hamiltonian as:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \frac{\hbar\omega}{2}(\hat{P}^2 + \hat{Q}^2) = \hbar\omega(\hat{b}^+\hat{b} + \frac{1}{2}) \tag{8}$$

so $A_H(t) = e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}$ and the Schrödinger operators for the transformed momentum and coordinates of the oscillator are $\hat{P} = \hat{p}/(\hbar\omega m)^{1/2}$ and $\hat{Q} = x(m\omega/\hbar)^{1/2}$, so $\hat{b} = (\hat{Q} + i\hat{P})/\sqrt{2}$, $\hat{b}^+ = (\hat{Q} - i\hat{P})/\sqrt{2}$, and $[\hat{b}, \hat{b}^+] = 1$

(b) Show that $\hat{Q}_H(t) = \hat{Q}\cos\omega t + \hat{P}\sin\omega t$.