Quantum dynamics, NWI-SM295, computer assignment 1

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Question 1: Numerical solution of quantum harmonic oscillator

The harmonic oscillator Hamiltonian $\hat{H}_0$ is given by

$$\hat{H}_0 = -\frac{1}{2\mu}\frac{d^2}{dx^2} + V(x), \tag{1}$$

with $V(x) = \frac{1}{2}kx^2$. Take $\mu = 1$ and $k = 1$. To solve the harmonic oscillator problem,

$$\hat{H}_0\phi_n(x) = \epsilon_n\phi(x) \tag{2}$$

numerically, the wave function is represented by its values $\phi(x_i)$ on a grid,

$$x_i = x_0 + i\Delta, \qquad \text{for } i = 1, 2, \ldots, n. \tag{3}$$

The potential energy is represented by a diagonal matrix with matrix elements

$$V_{ij} = V(x_i)\delta_{ij}. \tag{4}$$

1a. Use the second order finite difference approximation of d^2/dx^2 to set up a kinetic energy matrix.

1b. Find a grid such that the error in the lowest 4 eigenvalues is less than 1 %.

1c. Tabulate the eigenvalues and make a plot of the corresponding eigenvectors on the grid.

Question 2: Morse potential for HF

Find the spectroscopic constants of the electronic ground state of HF, e.g., on

`http://webbook.nist.gov/chemistry/form-ser.html`

Select "Constants of diatomic molecules". The electronic ground state is labeled by X. The rotation-vibration energy levels are represented by so called term values:

$$E_{v,J} = E_0 + G(v) + F_v(J), \tag{5}$$

for vibrational quantum numbers $v = 0, 1, \ldots$, and rotational quantum numbers $J = 0, 1, \ldots$. The vibrational term values are expanded as

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \ldots \tag{6}$$

and the v-dependent rotational term values as

$$F_v(J) = F_v(0) + B_v J(J+1) - D_v J^2 (J+1)^2, \tag{7}$$

where D_v is a rotational distortion constant. The rotational constant B_v is further expanded as

$$B_v = B_e - \alpha_e (v + \frac{1}{2}), \tag{8}$$

where α_e is a rotation-vibration coupling constant. A Morse potential is given by

$$V(r) = V_e + D_e [1 - e^{-\alpha(r - r_e)}]^2. \tag{9}$$

2a. Find the parameters D_e and α that give the best agreement with the experimental results for the rotational ground state ($J = 0$) of the first four vibrational levels. *Hint:* choose a value of D_e and use the analytic results of exercise 2 of week 1 to determine the α that reproduces the harmonic oscillator frequency ω_e. Compute numerically the first four vibrational energy levels and compare the differences with the spectroscopic result. Repeat for different choices of D_e.

2b. Determine r_e from the experimental value of B_e. Now try to predict the spectroscopic parameters α_e and D_0 using the Morse potential of the previous question by computing a few rotational levels for $v = 0$ and $v = 1$ and fitting the results with Eqs. (7) and (8). Compare the results to the experimental values.