Quantum Dynamics, NWI-SM295, exercises week 1

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Question 1: Separating center-of-mass motion

Two particles with Cartesian coordinates x_1 and x_2, and masses m_1 and m_2 move along a line. They are connected with a spring with force constant k. The equilibrium distance between the particles is r_0. The Hamiltonian for this system is given by

$$\hat{H} = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + \frac{1}{2}k(x_2 - x_1 - r_0)^2. \tag{1}$$

1a. Rewrite this Hamiltonian in coordinates X and y, where X is the center-of-mass coordinate and $y \equiv x_2 - x_1 - r_0$ and show that the Hamiltonian can be written as the sum of two parts

$$\hat{H} = \hat{T}(X) + \hat{H}_0(y). \tag{2}$$

In the new coordinates, the time-independent Schrödinger equation is given by

$$\hat{H}\Psi(y, X) = E\Psi(y, X). \tag{3}$$

To solve this equation, assume that the solution can be written as a product of a function describing the center-of-mass motion, $\chi(X)$ and a function describing the relative motion of the particles, $\phi(y)$,

$$\Psi(y, X) = \phi(y)\chi(X). \tag{4}$$

1b. Derive a time-independent Schrödinger equation for $\phi(y)$, assuming that the expectation value of the center-of-mass kinetic energy equals K,

$$\frac{\langle\chi(X)|\hat{T}(X)|\chi(X)\rangle}{\langle\chi|\chi\rangle} = K. \tag{5}$$

Question 2: The harmonic oscillator

The one-dimensional harmonic oscillator Hamiltonian is given by

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2} + \frac{1}{2}ky^2. \tag{6}$$

The harmonic oscillator wave functions $\phi_n(y)$ with energies E_n are solutions of the Schrödinger equation

$$\hat{H}_0\phi_n(y) = E_n\phi_n(y), \quad n = 0, 1, 2, \ldots \tag{7}$$

To solve this equation one may use the information on Hermite polynomials $H_n(x)$ (chapter 22, "orthogonal polynomials", of Ref. [1].).

The differential equation:

$$\left[\frac{\partial^2}{\partial x^2} + (2n + 1 - x^2)\right] H_n(x)e^{-\frac{1}{2}x^2} = 0, \tag{8}$$

the recursion relations

$$\begin{aligned} H_0(x) &= 1 && (9)\\ H_1(x) &= 2x && (10)\\ H_{n+1}(x) &= 2xH_n(x) - 2nH_{n-1}(x) \quad \text{for } n = 1, 2, \ldots && (11) \end{aligned}$$

and orthonormality

$$\int_{-\infty}^{+\infty} H_m^*(x)H_n(x)e^{-x^2}dx = 2^n n!\sqrt{\pi}\delta_{m,n} \tag{12}$$

2a. Find a suitable coordinate transformation $x = \alpha y$ to solve the Harmonic oscillator problem of Eq. (7) in terms of Hermite polynomials and normalize the solutions $\phi_n(y)$.

2b. Also find the energies E_n.

Question 3: Morse oscillator

The Morse potential a diatomic molecule is given by

$$V(r) = D_e[1 - e^{-\alpha(r-r_e)}]^2, \tag{13}$$

where r is the interatomic distance, D_e is the dissociation energy, r_e is the equilibrium distance and α is a parameter.

The radial Schrödinger equation for a diatomic molecule with rotational quantum number l and reduced mass μ is given by

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right]\chi_{v,l}(r) = E_{v,l}\chi_{v,l}(r). \tag{14}$$

3a. Derive an expression for $E_{v,l=0}$ in the harmonic approximation, i.e., for a molecule that is not rotating.

3b. Still using the harmonic approximation for the Morse potential, use first order perturbation theory to derive an expression for $E_{v,l}$ for other values of l.

Question 4: The harmonic oscillator, part II

Note: the first three questions prepare for the computerassignment. You can also do this question later.

4a. Use the recursion relations Eqs. (9-11) to show that

$$H_n(-x) = (-1)^n H_n(x). \tag{15}$$

4b. Use symmetry to show that

$$\langle\phi_n|y|\phi_n\rangle = 0. \tag{16}$$

4c. Use the recursion relation twice to write $x^2 H_n$ as a linear combination of Hermite polynomials.

4d. Use the last result and the orthonogonality of harmonic oscillator functions to compute the expectation value

$$\langle y^2\rangle = \frac{\langle\phi_n|y^2|\phi_n\rangle}{\langle\phi_n|\phi_n\rangle}.$$

References

[1] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, National Bureau of Standards, Washington, D.C., 1964.