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

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

Answer: *The C.O.M. coordinate is given by:*

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}. \tag{3}$$

Use the chain rule to rewrite $\frac{\partial}{\partial x_1}$ *and* $\frac{\partial}{\partial x_2}$*,*

$$\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial y}{\partial x_1}\frac{\partial}{\partial y} \tag{4}$$

$$= \frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial y} \tag{5}$$

so

$$\frac{\partial^2}{\partial x_1^2} = \left(\frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial y}\right)^2 \tag{6}$$

$$= \frac{m_1^2}{(m_1 + m_2)^2}\frac{\partial^2}{\partial X^2} - \frac{2m_1}{m_1 + m_2}\frac{\partial^2}{\partial X \partial y} + \frac{\partial^2}{\partial y^2} \tag{7}$$

In the same way we get

$$\frac{\partial^2}{\partial x_2^2} = \frac{m_2^2}{(m_1 + m_2)^2}\frac{\partial^2}{\partial X^2} + \frac{2m_2}{m_1 + m_2}\frac{\partial^2}{\partial X \partial y} + \frac{\partial^2}{\partial y^2}. \tag{8}$$

Thus, for the kinetic energy part of the Hamiltonian $\hat{H}$ *we have*

$$-\frac{\hbar^2}{2}\left(\frac{1}{m_1}\frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2}{\partial x_2^2}\right) = -\frac{\hbar^2}{2}\left[\frac{1}{m_1 + m_2}\frac{\partial^2}{\partial X^2} + \left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial y^2}\right]. \tag{9}$$

So we have the C.O.M. kinetic energy

$$\hat{T}(X) = -\frac{\hbar^2}{2(m_1 + m_2)}\frac{\partial^2}{\partial X^2} \tag{10}$$

and the harmonic oscillator Hamiltonian for coordinate y

$$\hat{H}_0(y) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2} + \frac{1}{2}ky^2, \tag{11}$$

where the reduced mass is defined by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}. \tag{12}$$

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

$$\hat{H}\Psi(y, X) = E\Psi(y, X). \tag{13}$$

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, $\phi(y)$,

$$\Psi(y, X) = \phi(y)\chi(X). \tag{14}$$

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

$$\frac{\langle\chi(X)|\hat{T}(X)|\chi(X)\rangle}{\langle\chi|\chi\rangle} = K. \tag{15}$$

Answer: *Substitute the Hamiltonian (Eq. 2) and wave function ansats (Eq. 14) into the Schrödinger equation (13).*

$$(\hat{T} + \hat{H}_0 - E)\phi(y)\chi(X) = 0, \tag{16}$$

and project onto χ

$$\int_{X=-\infty}^{\infty} dX\, \chi^*(X)(\hat{T} + \hat{H}_0 - E)\phi(y)\chi(X) = \langle\chi|\hat{T}|\chi\rangle\phi(y) + \langle\chi|\chi\rangle\hat{H}_0\phi(y) - E\langle\chi|\chi\rangle\phi(y) = 0. \tag{17}$$

If we devide the last equation by $\langle\chi|\chi\rangle$ *we get*

$$\hat{H}_0\phi(y) = (E - K)\phi(y). \tag{18}$$

Note that $E - K$ *is the total energy (*E*) minus the kinetic energy of the C.O.M. (*K*), so* $E - K$ *is the energy associated with the "internal motion" as described by coordinate* y*.*

Question 2: The harmonic oscillator

The one-dimensional harmonic oscillator Hamiltonian is given by

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2} + \frac{1}{2}ky^2. \tag{19}$$

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

$$\hat{H}_0\phi_n(y) = E_n\phi_n(y), \quad n = 0, 1, 2, \ldots \tag{20}$$

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:

$$\left[\frac{\partial^2}{\partial x^2} + (2n + 1 - x^2)\right] H_n(x)e^{-\frac{1}{2}x^2} = 0, \tag{21}$$

the recursion relations

$$\begin{aligned} H_0(x) &= 1 && (22)\\ H_1(x) &= 2x && (23)\\ H_{n+1}(x) &= 2xH_n(x) - 2nH_{n-1}(x) \quad \text{for } n = 1, 2, \ldots && (24) \end{aligned}$$

and orthonormality

$$\int_{-\infty}^{+\infty} H_m^*(x)H_n(x)e^{-x^2}dx = 2^n n!\sqrt{\pi}\delta_{m,n} \tag{25}$$

2a. Find a suitable coordinate transformation $x = \alpha y$ to solve the Harmonic oscillator problem of Eq. (20) in terms of Hermite polynomials and normalize the solutions $\phi_n(y)$.

Answer: *Rewrite Hamiltonian* $\hat{H}_0$ *in terms of* $x = \alpha y$*. For the kinetic energy operator use*

$$\frac{\partial}{\partial y} = \frac{\partial x}{\partial y}\frac{\partial}{\partial x} = \alpha\frac{\partial}{\partial x} \tag{26}$$

so

$$\frac{\partial^2}{\partial y^2} = \alpha^2 \frac{\partial^2}{\partial x^2} \tag{27}$$

and we can rewrite

$$\hat{H}_0 - E_n = -\frac{\hbar^2\alpha^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{k}{2\alpha^2}x^2 - E_n \tag{28}$$

$$= -\frac{\hbar^2\alpha^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} - \underbrace{\frac{2\mu k}{2\hbar^2\alpha^4}}_{=1}x^2 + \underbrace{\frac{2\mu E_n}{\hbar^2\alpha^2}}_{=2n+1}\right). \tag{29}$$

We assigned the factors so that the x-dependent operator matches Eq. (21), so we found

$$\frac{2\mu k}{2\hbar^2\alpha^4} = 1, \tag{30}$$

$$\frac{2\mu E_n}{\hbar^2\alpha^2} = 2n+1. \tag{31}$$

We can solve the first equation to find α,

$$\alpha^2 = \frac{1}{\hbar}\sqrt{\mu k}. \tag{32}$$

2b. Also find the energies E_n.

Answer: *Combining Eqs. (32) and (31) we get*

$$E_n = \frac{\hbar^2\alpha^2}{2\mu}(2n+1) = (n+\frac{1}{2})\hbar\omega, \quad \textit{with } \omega = \sqrt{\tfrac{k}{\mu}}. \tag{33}$$

Question 3: Morse oscillator

The Morse potential a diatomic molecule is given by

$$V(r) = D_e[1 - e^{-\alpha(r-r_e)}]^2, \tag{34}$$

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

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right]\chi_{v,l}(r) = E_{v,l}\chi_{v,l}(r). \tag{35}$$

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

Answer: *The minimum of the Morse potential is at $r = r_e$. The harmonic approximation is thus*

$$V_0(r) = \frac{1}{2}k(r-r_e)^2 \tag{36}$$

with

$$k = \frac{\partial^2 V(r)}{\partial r^2}|_{r=r_e} = 2\alpha D_e \frac{\partial}{\partial r}[(1-e^{-\alpha(r-r_e)})]|_{r=r_e} = 2\alpha^2 D_e. \tag{37}$$

The energy levels of the harmonic oscillator are $(n+\frac{1}{2})\hbar\omega$, with $\omega = \sqrt{k/\mu}$, so

$$E_{n,l=0} = \left(n+\frac{1}{2}\right)\hbar\alpha\sqrt{\frac{2D_e}{\mu}}. \tag{38}$$

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.

Answer: *In first order perturbation theory we partition the Hamiltonian in a zeroth order Hamiltonian $\hat{H}_0$ plus a perturbation V_1. We take the $l = 0$ Hamiltonian as $\hat{H}_0$, and the centrifugal term as perturbation. The first order perturbed energy is*

$$E_l^{(1)} = \langle \Psi_n^{(0)} | \frac{\hbar^2 l(l+1)}{2\mu r^2} | \Psi_n^{(0)} \rangle = \frac{\hbar^2 l(l+1)}{2\mu} \langle \Psi_n^{(0)} | \frac{1}{r^2} | \Psi_n^{(0)} \rangle. \tag{39}$$

where $\Psi_n^{(0)}$ is the Harmonic oscillator solution. The harmonic oscillator functions are centered around $r = r_e$, so we could estimate the expectation value from

$$\frac{1}{r^2} \approx \frac{1}{r_e^2}. \tag{40}$$

To be a little more accurate we can use an expansion $r = r_e + x$,

$$\frac{1}{r^2} = \frac{1}{(r_e + x)^2} = \frac{1}{r_e^2 + 2xr_e + x^2} = \frac{1}{r_e^2(1 + 2x/r_e + x^2/r_e^2)}. \tag{41}$$

Assuming x is small compared to r_e in the region where $\Psi_n^{(0)}$ is nonnegligible we can use the Taylor series

$$\frac{1}{1-z} = 1 + z + z^2 + \dots \tag{42}$$

with $z = -2x/r_e - x^2/r_e^2$, so to second order in x we have

$$\frac{1}{r^2} = \frac{1}{r_e^2} \left(1 \underbrace{- \frac{2x}{r_e} - \frac{x^2}{r_e^2}}_{z} + 4\frac{x^2}{r_e^2} \right). \tag{43}$$

*In the harmonic oscillator approximation the expectation value of the term linear in x is zero, but we can use the analytic result of the previous question (**3a**) to compute $\langle x^2 \rangle$.*

Another, probaby more accurate way to approximate the result for nonzero l is to make the harmonic approximation for the effective potential, i.e., the sum of the Morse potential and the centrifugal term.

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. (22-24) to show that

$$H_n(-x) = (-1)^n H_n(x). \tag{44}$$

Answer: *From Eqs. (22) and (23) we see that the relation holds for $n = 0$ and for $n = 1$. Assuming the relation holds for H_n and H_{n-1}, then we find for H_{n+1}*

$$\begin{aligned} H_{n+1}(-x) &= 2(-x)H_n(-x) - 2nH_{n-1}(-x) && (45)\\ &= (-1)^{n+1}[2xH_n(x) - 2nH_{n-1}(x)] && (46)\\ &= (-1)^{n+1}H_{n+1}(x), && (47) \end{aligned}$$

so recursively we find that it holds for all $n \geq 0$.

4b. Use symmetry to show that

$$\langle \phi_n | y | \phi_n \rangle = 0. \tag{48}$$

Answer: *First we define a symmetry operator that changes the sign of y*

$$\hat{\imath} y = -y, \tag{49}$$

so

$$\hat{\imath}\phi_n(y) = \phi_n(-y) = (-1)^n \phi(n)(y). \tag{50}$$

Since $\hat{\imath}^2 = 1$ *we have* $\hat{\imath}^{-1} = \hat{\imath}$, *and since symmetry operators are unitary, we also have* $\hat{\imath}^\dagger = \hat{\imath}^{-1} = \hat{\imath}$, *so*

$$\begin{aligned} \langle \phi_n | y | \phi_n \rangle &= \langle \phi_n | \hat{\imath}^\dagger \hat{\imath} y | \phi_n \rangle & (51)\\ &= \langle \hat{\imath}\phi_n | \hat{\imath} y | \phi_n \rangle & (52)\\ &= \langle (-1)^n \phi_n | (-1)^{n+1} y | \phi_n \rangle & (53)\\ &= (-1)^{2n+1} \langle \phi_n | y | \phi_n \rangle & (54)\\ &= -\langle \phi_n | y | \phi_n \rangle. & (55) \end{aligned}$$

so

$$2\langle \phi_n | y | \phi_n \rangle = 0. \tag{56}$$

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

Answer: *Equation 24 can be rewritten as*

$$xH_n(x) = \frac{1}{2}H_{n+1}(x) + nH_{n-1}(x), \tag{57}$$

so we also have

$$\begin{aligned} xH_{n+1}(x) &= \frac{1}{2}H_{n+2}(x) + (n+1)H_n(x) & (58)\\ xH_{n-1}(x) &= \frac{1}{2}H_n(x) + (n-1)H_{n-2}(x) & (59) \end{aligned}$$

and

$$\begin{aligned} x^2 H_n(x) &= \frac{1}{2}xH_{n+1}(x) + nxH_{n-1}(x) & (60)\\ &= \frac{1}{4}H_{n+2}(x) + \frac{1}{2}(n+1)H_n(x) \;+\; n[\frac{1}{2}H_n(x) + (n-1)H_{n-2}(x)] & (61)\\ &= \frac{1}{4}H_{n+2}(x) + (n+\frac{1}{2})H_n(x) + n(n-1)H_{n-2}(x). & (62) \end{aligned}$$

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

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

Answer: *For* $\alpha = 1$ *we have* $y = x$ *and the result would be*

$$\langle x^2 \rangle = n + \frac{1}{2}. \tag{63}$$

Since $y = x/\alpha$ *we have*

$$y^2 = \frac{\hbar}{\sqrt{\mu k}}x^2 = \frac{\hbar}{\mu\omega}x^2 \tag{64}$$

or

$$\langle y^2 \rangle = \frac{\hbar}{\mu\omega}(n + \frac{1}{2}). \tag{65}$$

To see if this is reasonable, we can use this result to compute the expectation value of the potential energy

$$\langle \frac{1}{2} k y^2 \rangle = \frac{1}{2} k \langle y^2 \rangle = \frac{1}{2} \hbar\omega (n + \frac{1}{2}) = \frac{1}{2} E_n, \tag{66}$$

where we used $\omega = \sqrt{k/\mu}$ *in the second step. So we find that the expectation value of the potential energy for* ϕ_n *is half of the energy of that state* E_n*. Thus, the expectation value of the kinetic energy must als be half of* E_n*. This is known as the virial theorem for the harmonic oscillator.*

References

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