Ch126
Winter Quarter – 2024
Problem Set 2

Due: 18 January, 2024

1 Problem 1

(20 points) Adjoint operators are defined in terms of their expectation values. Two operators $\hat{G}$ and $\hat{G}^\dagger$ are adjoint if their expectation values are complex conjugates of each other, i.e.:

$$\langle \Phi | \hat{G}^\dagger \Phi \rangle = \langle \Phi | \hat{G} \Phi \rangle^* \tag{1}$$

and

$$(\hat{G}^\dagger)^\dagger = \hat{G} \tag{2}$$

(the dagger indicates the adjoint; the asterisk indicates the complex conjugate of a number).

For adjoint operators $\hat{G}$ and $\hat{G}^\dagger$ you have proven the turnover rule:

$$\langle \phi_1 | \hat{G}^\dagger | \phi_2 \rangle = \langle \hat{G} \phi_1 | \phi_2 \rangle \tag{3}$$

The turnover rule is extremely useful for finding the adjoint of a given operator.

The linear momentum operator in one dimension is:

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} \tag{4}$$

Use the following integral I, the method of integration by parts, and the turnover rule to find the adjoint of the linear momentum operator, $\hat{p}^\dagger$.

$$I = \langle \hat{p} \phi_1 | \phi_2 \rangle = \int_{-\infty}^{+\infty} \left(\frac{\hbar}{i} \frac{\partial \phi_1}{\partial x} \right)^* \phi_2 \, dx \tag{5}$$

Assume that the wavefunctions ϕ_1 and ϕ_2 and their complex conjugates vanish at $\pm\infty$.

1.1 Answer

We can use integration by parts to solve this integral, with $u = \phi_2$ and $dv = \left(\frac{\hbar}{i}\frac{\partial \phi_1}{\partial x}\right)^* dx$, so $du = \frac{\partial \phi_2}{\partial x} dx$ and $v = -\frac{\hbar}{i}\phi_1^*$, and we get:

$$I = \langle \hat{p}\phi_1|\phi_2\rangle = \int_{-\infty}^{+\infty} \left(\frac{\hbar}{i}\frac{\partial \phi_1}{\partial x}\right)^* \phi_2 \, dx \tag{6}$$

$$= \left[-\frac{\hbar}{i}\phi_1^*\phi_2\right]_{-\infty}^{+\infty} + \int_{-\infty}^{+\infty} \frac{\hbar}{i}\phi_1^*\frac{\partial \phi_2}{\partial x} \, dx \tag{7}$$

We know that the wavefunctions ϕ_1 and ϕ_2 vanish at $\pm\infty$, so the first term in the equation above is zero, and we get:

$$I = -\int_{-\infty}^{+\infty} \frac{\hbar}{i}\phi_1^*\frac{\partial \phi_2}{\partial x} \, dx \tag{8}$$

Rearranging this equation:

$$I = \int_{-\infty}^{+\infty} \frac{\hbar}{i}\frac{\partial \phi_2}{\partial x}\phi_1^* \, dx \tag{9}$$

Putting this into bra-ket notation:

$$I = \langle \phi_1|\hat{p}|\phi_2\rangle \tag{10}$$

So, we have found that:

$$\langle \hat{p}\phi_1|\phi_2\rangle = \langle \phi_1|\hat{p}|\phi_2\rangle = \langle \phi_1|\hat{p}^\dagger|\phi_2\rangle \tag{11}$$

2 Problem 2

(20 points) Consider the set of angular momentum functions $|j, m\rangle$ that are eigenfunctions of the operators $\hat{j}^2$ and $\hat{j}_z$. Matrix elements of an arbitrary operator $\hat{O}$ in this basis set in this basis set have the form:

$$O_{mm'} = \langle j, m|\hat{O}|j, m'\rangle$$

The operator $\hat{O}$ in this basis set can be represented by a $(2j + 1) \times (2j + 1)$ matrix with rows labeled by m and columns labeled by m'.

2.1 Part (a)

For the case $j = 1$, write down explicitly the 3×3 matrices representing the operators $\hat{j}^2$, $\hat{j}_z$, $\hat{j}_+$, $\hat{j}_-$, $\hat{j}_x$, and $\hat{j}_y$.

2.1.1 Answer

For the case $j = 1$, we have $m = -1, 0, 1$. We note that the convention is to transfers the matrix from left to right with $m = 1, 0, -1$. First, we know when operating $\hat{j}^2$ on $|j,m\rangle$, we get:

$$\hat{j}^2 |j,m\rangle = j(j+1)\hbar^2 |j,m\rangle \tag{12}$$

So, the matrix representation is independent of m, and we get:

$$\hat{j}^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{13}$$

Now, we know when operating $\hat{j}_z$ on $|j,m\rangle$, we get:

$$\hat{j}_z |j,m\rangle = m\hbar |j,m\rangle \tag{14}$$

So, the matrix representation is:

$$\hat{j}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{15}$$

Now, we know when operating $\hat{j}_+$ on $|j,m\rangle$, we get:

$$\hat{j}_+ |j,m\rangle = \hbar\sqrt{j(j+1) - m(m+1)}\, |j,m+1\rangle \tag{16}$$

So, that factor is of the form $\hbar\sqrt{2 - m(m+1)}$, and we only care about the $m = -1, 0$ terms on the column for the ket, so we get:

$$\hat{j}_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \tag{17}$$

Now, we know when operating $\hat{j}_-$ on $|j,m\rangle$, we get:

$$\hat{j}_- |j,m\rangle = \hbar\sqrt{j(j+1) - m(m-1)}\, |j,m-1\rangle \tag{18}$$

So, that factor is of the form $\hbar\sqrt{2 - m(m-1)}$, and we only care about the $m = 0, 1$ terms on the column for the ket, so we get:

$$\hat{j}_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix} \tag{19}$$

Now, we know $\hat{j}_x$ is defined as:

$$\hat{j}_x = \frac{1}{2}\left(\hat{j}_+ + \hat{j}_-\right) \tag{20}$$

So, we can add the matrices from above, and we get:

$$\hat{j}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix} \tag{21}$$

Now, we know $\hat{j}_y$ is defined as:

$$\hat{j}_y = \frac{1}{2i}\left(\hat{j}_+ - \hat{j}_-\right) \tag{22}$$

So, we can subtract the matrices from above, and we get:

$$\hat{j}_y = \frac{\hbar}{2i}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ -\sqrt{2} & 0 & \sqrt{2} \\ 0 & -\sqrt{2} & 0 \end{pmatrix} \tag{23}$$

2.2 Part (b)

Use the matrices from (a) to prove the following commutators:

$$[\hat{j}_x, \hat{j}_y] = i\hbar\hat{j}_z, \quad [\hat{j}_y, \hat{j}_z] = i\hbar\hat{j}_x, \quad [\hat{j}_z, \hat{j}_x] = i\hbar\hat{j}_y$$

2.2.1 Answer

We will start with the first commutator:

$$[\hat{j}_x, \hat{j}_y] = \hat{j}_x\hat{j}_y - \hat{j}_y\hat{j}_x \tag{24}$$

We can substitute in the matrices from part (a), and we get:

$$[\hat{j}_x, \hat{j}_y] = \frac{\hbar^2}{4i}\begin{pmatrix} -2 & 0 & 2 \\ 0 & 0 & 0 \\ -2 & 0 & 2 \end{pmatrix} - \frac{\hbar^2}{4i}\begin{pmatrix} 2 & 0 & 2 \\ 0 & 0 & 0 \\ -2 & 0 & -2 \end{pmatrix} \tag{25}$$

$$= \frac{\hbar^2}{4i}\begin{pmatrix} -4 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 4 \end{pmatrix} = i\hbar^2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{26}$$

$$= i\hbar\hat{j}_z \tag{27}$$

That attached SymPy script gives:

$$[\hat{j}_y, \hat{j}_z] = \frac{i\sqrt{2}\hbar^2}{2}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = i\hbar\hat{j}_x \tag{28}$$

$$\tag{29}$$

and finally:

$$[\hat{j}_z, \hat{j}_x] = \frac{\sqrt{2}\hbar^2}{2} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} = i\hbar\hat{j}_y \tag{30}$$

Result: Verify the commutators

```
from sympy import Matrix, I, sqrt, symbols
hbar = symbols('hbar')
j_x = (hbar*sqrt(2)/2)*Matrix([[0, 1, 0],
                 [1, 0, 1],
                 [0, 1, 0]])

j_y = (hbar*sqrt(2)/(2*I))*Matrix([[0, 1, 0],
                    [-1, 0, 1],
                    [0, -1, 0]])

j_z = hbar*Matrix([[1, 0, 0],
                    [0, 0, 0],
                    [0, 0, -1]])

# evaluate the commutators
print("Commutator of Jx and Jy:")
print((j_x*j_y - j_y*j_x).doit())
print("Commutator of Jy and Jz:")
print((j_y*j_z - j_z*j_y).doit())
print("Commutator of Jz and Jx:")
print((j_z*j_x - j_x*j_z).doit())
```

Algorithm 1: SymPy script to verify the commutators

3 Problem 3

(20 points) Two-state energy transfer. Assume that two identical, well-separated molecules, A and B, have excited states described by the wavefunctions $\Psi_A(q,t) = \psi_A(q)e^{-iE_At/\hbar}$ and $\Psi_B(q,t) = \psi_B(q)e^{-iE_Bt/\hbar}$, respectively. Assume that $\psi_A(q)$ and $\psi_B(q)$ are orthonormal eigenfunctions of the Hamiltonian $\hat{H}^0$ where:

$$\hat{H}^0|\psi_A(q)\rangle = E_A|\psi_A(q)\rangle,$$
$$\hat{H}^0|\psi_B(q)\rangle = E_B|\psi_B(q)\rangle.$$

Since the molecules are identical, $E_A = E_B = E_0$. If A and B are brought into close proximity, there will be an interaction between them described by the time-independent perturbation operator $\hat{H}'$ with the following matrix elements:

$$\langle\psi_A(q)|\hat{H}'|\psi_A(q)\rangle = \langle\psi_B(q)|\hat{H}'|\psi_B(q)\rangle = 0,$$
$$\langle\psi_A(q)|\hat{H}'|\psi_B(q)\rangle = \langle\psi_B(q)|\hat{H}'|\psi_A(q)\rangle = \gamma.$$

A general state of this two-molecule system can be described by the superposition wavefunction $|t\rangle$:

$$|t\rangle = C_A|\psi_A(q)\rangle e^{-iE_0t/\hbar} + C_B|\psi_B(q)\rangle e^{-iE_0t/\hbar},$$

where the coefficients C_A and C_B are functions of time. Since the zero of energy is arbitrary, it is convenient to define $E_0 = 0$.

3.1 Part (a)

Use the definition of $|t\rangle$ in the time-dependent Schrödinger equation with the Hamiltonian $\hat{H} = \hat{H}^0 + \hat{H}'$ to generate an equation relating the time derivatives of C_A and C_B (denoted as $\dot{C}_A$ and $\dot{C}_B$) to C_A and C_B.

3.1.1 Answer

The time-dependent Schrödinger equation is given by:

$$i\hbar\frac{\partial}{\partial t}|t\rangle = \hat{H}|t\rangle \tag{31}$$

First, we will only focus on the left and side, and substituting in for $|t\rangle$ and taking out the exponential term, which is a common factor, we get:

$$i\hbar\frac{\partial}{\partial t}|t\rangle = i\hbar\left(\dot{C}_A|\psi_A(q)\rangle + C_A|\psi_A(q)\rangle\left(-\frac{iE_0}{\hbar}\right) + \dot{C}_B|\psi_B(q)\rangle + C_B|\psi_B(q)\rangle\left(-\frac{iE_0}{\hbar}\right)\right)e^{-iE_0t/\hbar} \tag{32}$$

Now, we will focus on the right hand side of the equation, and substituting in for $|t\rangle$ gives:

$$\hat{H}|t\rangle = \left(\hat{H}^0 + \hat{H}'\right)\left(C_A|\psi_A(q)\rangle e^{-iE_0t/\hbar} + C_B|\psi_B(q)\rangle e^{-iE_0t/\hbar}\right) \tag{33}$$
$$= \left(\hat{H}^0 + \hat{H}'\right)\left(C_A|\psi_A(q)\rangle + C_B|\psi_B(q)\rangle\right)e^{-iE_0t/\hbar} \tag{34}$$

We can cancel the exponential term from both sides, and we get:

$$i\hbar\frac{\partial}{\partial t}|t\rangle = \left(\hat{H}^0 + \hat{H}'\right)\left(C_A|\psi_A(q)\rangle + C_B|\psi_B(q)\rangle\right) \tag{35}$$

Now, we distribute the Hamiltonian to the terms inside the parenthesis:

$$i\hbar\frac{\partial}{\partial t}|t\rangle = \left(\hat{H}^0 + \hat{H}'\right)\left(C_A|\psi_A(q)\rangle + C_B|\psi_B(q)\rangle\right) \tag{36}$$
$$= \left(\hat{H}^0C_A|\psi_A(q)\rangle + \hat{H}^0C_B|\psi_B(q)\rangle + \hat{H}'C_A|\psi_A(q)\rangle + \hat{H}'C_B|\psi_B(q)\rangle\right) \tag{37}$$

The first two terms are just they eigenvalue equations for $\hat{H}^0$, so we can simplify the equation to:

$$i\hbar\frac{\partial}{\partial t}|t\rangle = \Big(E_A C_A|\psi_A(q)\rangle + E_B C_B|\psi_B(q)\rangle + \hat{H}' C_A|\psi_A(q)\rangle + \hat{H}' C_B|\psi_B(q)\rangle\Big) \tag{38}$$

Now, we equate the left and right hand sides of the equation, and we get:

$$\Big(i\hbar\dot{C}_A|\psi_A(q)\rangle + E_0 C_A|\psi_A(q)\rangle + i\hbar\dot{C}_B|\psi_B(q)\rangle + E_0 C_B|\psi_B(q)\rangle\Big) \tag{39}$$

$$= \Big(E_A C_A|\psi_A(q)\rangle + E_B C_B|\psi_B(q)\rangle + \hat{H}' C_A|\psi_A(q)\rangle + \hat{H}' C_B|\psi_B(q)\rangle\Big) \tag{40}$$

3.2 Part (b)

Left multiply the result from (a) by $\langle\psi_A(q)|$ to get a differential equation for $\dot{C}_A$.

3.2.1 Answer

Multiplying by $\langle\psi_A(q)|$ gives:

$$\langle\psi_A(q)|\Big(i\hbar\dot{C}_A|\psi_A(q)\rangle + E_0 C_A|\psi_A(q)\rangle + i\hbar\dot{C}_B|\psi_B(q)\rangle + E_0 C_B|\psi_B(q)\rangle\Big) \tag{41}$$

$$= \langle\psi_A(q)|\Big(E_A C_A|\psi_A(q)\rangle + E_B C_B|\psi_B(q)\rangle + \hat{H}' C_A|\psi_A(q)\rangle + \hat{H}' C_B|\psi_B(q)\rangle\Big) \tag{42}$$

We can simplify the left side of the equation by using the orthonormality of the eigenfunctions of $\hat{H}^0$, and we get:

$$\langle\psi_A(q)|\Big(i\hbar\dot{C}_A|\psi_A(q)\rangle + E_0 C_A|\psi_A(q)\rangle + i\hbar\dot{C}_B|\psi_B(q)\rangle + E_0 C_B|\psi_B(q)\rangle\Big) \tag{43}$$

$$= i\hbar\dot{C}_A + E_0 C_A \tag{44}$$

The right hand side gives:

$$\langle\psi_A(q)|\Big(E_A C_A|\psi_A(q)\rangle + E_B C_B|\psi_B(q)\rangle + \hat{H}' C_A|\psi_A(q)\rangle + \hat{H}' C_B|\psi_B(q)\rangle\Big) \tag{45}$$

$$= E_A C_A + \gamma C_B \tag{46}$$

Now, we can equate the left and right hand sides of the equation, and we get:

$$i\hbar\dot{C}_A + E_0 C_A = E_A C_A + \gamma C_B \tag{47}$$

3.3 Part (c)

Left multiply the result from (a) by $\langle\psi_B(q)|$ to get a differential equation for $\dot{C}_B$.

3.3.1 Answer

We implement the same procedure as before:

$$\langle\psi_B(q)|\left(i\hbar\dot{C}_A|\psi_A(q)\rangle + E_0C_A|\psi_A(q)\rangle + i\hbar\dot{C}_B|\psi_B(q)\rangle + E_0C_B|\psi_B(q)\rangle\right) \tag{48}$$

$$= \langle\psi_B(q)|\left(E_AC_A|\psi_A(q)\rangle + E_BC_B|\psi_B(q)\rangle + \hat{H}'C_A|\psi_A(q)\rangle + \hat{H}'C_B|\psi_B(q)\rangle\right) \tag{49}$$

We can simplify the left side of the equation by using the orthonormality of the eigenfunctions of $\hat{H}^0$, and we get:

$$\langle\psi_B(q)|\left(i\hbar\dot{C}_A|\psi_A(q)\rangle + E_0C_A|\psi_A(q)\rangle + i\hbar\dot{C}_B|\psi_B(q)\rangle + E_0C_B|\psi_B(q)\rangle\right) \tag{50}$$

$$= i\hbar\dot{C}_B + E_0C_B \tag{51}$$

The right hand side gives:

$$\langle\psi_B(q)|\left(E_AC_A|\psi_A(q)\rangle + E_BC_B|\psi_B(q)\rangle + \hat{H}'C_A|\psi_A(q)\rangle + \hat{H}'C_B|\psi_B(q)\rangle\right) \tag{52}$$

$$= E_BC_B + \gamma C_A \tag{53}$$

Now, we can equate the left and right hand sides of the equation, and we get:

$$i\hbar\dot{C}_B + E_0C_B = E_BC_B + \gamma C_A \tag{54}$$

3.4 Part (d)

Exercises (b) and (c) will give two coupled first order differential equations. They can be solved by taking the time-derivative of the (b) result, then substituting the (c) result to get a second-order linear differential equation with constant coefficients. Derive the second-order linear differential equation for C_A.

3.4.1 Answer

We take the time derivative of the result from part (b):

$$i\hbar\ddot{C}_A + E_0\dot{C}_A = E_A\dot{C}_A + \gamma\dot{C}_B \tag{55}$$

We isolate the $\dot{C}_B$ term from the result from part (c):

$$\dot{C}_B = \frac{1}{i\hbar}\left(E_0C_B - E_BC_B + \gamma C_A\right) \tag{56}$$

We substitute this into the equation above, and we get:

$$i\hbar\ddot{C}_A + E_0\dot{C}_A = E_A\dot{C}_A + \gamma\left(\frac{1}{i\hbar}\left(E_0C_B - E_BC_B + \gamma C_A\right)\right) \tag{57}$$

We are able to assume that $E_A = E_B = E_0$, so we can simplify the equation to:

$$i\hbar\ddot{C}_A = \gamma^2\left(\frac{1}{i\hbar}C_A\right) \tag{58}$$

We can simplify the equation further by dividing both sides by $i\hbar$:

$$\boxed{\ddot{C}_A = -\left(\frac{\gamma}{\hbar}\right)^2 C_A} \tag{59}$$

We want to do the same thing, but for C_B, so we take the time derivative of the result from part (c):

$$i\hbar\ddot{C}_B + E_0\dot{C}_B = E_B\dot{C}_B + \gamma\dot{C}_A \tag{60}$$

We isolate the $\dot{C}_A$ term from the result from part (b):

$$\dot{C}_A = \frac{1}{i\hbar}\left(E_0C_A - E_AC_A + \gamma C_B\right) \tag{61}$$

We substitute this into the equation above, and we get:

$$i\hbar\ddot{C}_B + E_0\dot{C}_B = E_B\dot{C}_B + \gamma\left(\frac{1}{i\hbar}\left(E_0C_A - E_AC_A + \gamma C_B\right)\right) \tag{62}$$

We are able to assume that $E_A = E_B = E_0$, so we can simplify the equation to:

$$i\hbar\ddot{C}_B = \gamma^2\left(\frac{1}{i\hbar}C_B\right) \tag{63}$$

We can simplify the equation further by dividing both sides by $i\hbar$:

$$\boxed{\ddot{C}_B = -\left(\frac{\gamma}{\hbar}\right)^2 C_B} \tag{64}$$

3.5 Part (e)

The most general solution to second-order differential equations of the type: $\ddot{u} = -a^2u$ is $u = Q\sin(at) + R\cos(at)$. Find general solutions for the time-dependent coefficients C_A and C_B.

3.5.1 Answer

We have $u = C_A$ and $a = \frac{\gamma}{\hbar}$, so we can substitute these into the equation above, and we get:

$$C_A = Q \sin\left(\frac{\gamma}{\hbar}t\right) + R\cos\left(\frac{\gamma}{\hbar}t\right) \tag{65}$$

We have $u = C_B$ and $a = \frac{\gamma}{\hbar}$, so we can substitute these into the equation above, and we get:

$$C_B = S \sin\left(\frac{\gamma}{\hbar}t\right) + T\cos\left(\frac{\gamma}{\hbar}t\right) \tag{66}$$

3.6 Part (f)

Use the normalization condition for $|t\rangle$ and the initial condition that molecule A was excited at $t = 0$ (i.e., $C_A^*(0)C_A(0) = 1$) and molecule B is not excited at $t = 0$ (i.e., $C_B^*(0)C_B(0) = 0$) to obtain expressions for C_A and C_B.

3.6.1 Answer

As the system evolves in time, the coefficients $C_A(t)$ and $C_B(t)$ will change, but they must always satisfy the normalization condition. Therefore, at any time t:

$$|C_A(t)|^2 + |C_B(t)|^2 = 1 \tag{67}$$

Using the differential equations derived in parts (d) and (e), and the initial conditions, we can solve for $C_A(t)$ and $C_B(t)$. For example, if $C_A(0) = 1$ and $\dot{C}_A(0) = 0$ (since molecule B is not initially excited and there is no initial motion between states), the solution for $C_A(t)$ will be of the form with $R = 1$ and $Q = 0$:

$$\boxed{C_A(t) = \cos\left(\frac{\gamma}{\hbar}t\right)} \tag{68}$$

$$\boxed{C_B(t) = \sin\left(\frac{\gamma}{\hbar}t\right)} \tag{69}$$