Ch126
Winter Quarter – 2024
Problem Set 2
Due: 18 January, 2024

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.:

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

and

$$\left(\hat{G}^\dagger\right)^\dagger = \hat{G}$$

(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:

$$\langle\varphi_1|\hat{G}^\dagger|\varphi_2\rangle = \langle\hat{G}\varphi_1|\varphi_2\rangle$$

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

The linear momentum operator in one dimension is:

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

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

$$I = \langle\hat{p}\varphi_1|\varphi_2\rangle = \int_{-\infty}^{+\infty}\left(\frac{\hbar}{i}\frac{\partial\varphi_1}{\partial x}\right)^* \varphi_2 dx$$

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

2. (20 points) Consider the set of angular momentum functions $|j,m\rangle$ that are eigenfunctions of the operators $\hat{\boldsymbol{j}}^2$ 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)×(2j+1) matrix with rows labeled by m and columns labeled by m'.

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

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

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

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

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

3. (20 points) Two-state energy transfer. Assume that two identical, well-separated molecules, A and B, have excited states described by the wavefunctions $\Psi_A(q,t) = \psi_A(q)e^{-iE_A t/\hbar}$ and $\Psi_B(q,t) = \psi_B(q)e^{-iE_B t/\hbar}$, respectively. Assume that $\psi_A(q)$ and $\psi_B(q)$ are orthonormal eigenfunctions of the Hamiltonian $\widehat{H}^0$ where:

$$\widehat{H}^0|\psi_A(q)\rangle = E_A|\psi_A(q)\rangle$$

and

$$\widehat{H}^0|\psi_B(q)\rangle = E_B|\psi_B(q)\rangle$$

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

$$\langle\psi_A(q)|\widehat{H}'|\psi_A(q)\rangle = \langle\psi_B(q)|\widehat{H}'|\psi_B(q)\rangle = 0$$

and

$$\langle\psi_A(q)|\widehat{H}'|\psi_B(q)\rangle = \langle\psi_B(q)|\widehat{H}'|\psi_A(q)\rangle = \gamma$$

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

$$|\mathrm{t}\rangle = C_A|\psi_A(q)\rangle e^{-iE_0 t/\hbar} + C_B|\psi_B(q)\rangle e^{-iE_0 t/\hbar}$$

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

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

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

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

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.

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

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.