Molecular quantum dynamics: Solutions 1

Problem 1: Two-level quantum dynamics

(a)

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle \tag{1}$$
$$= \frac{1}{2}e^{-i\hat{H}t/\hbar}|\psi_0\rangle + \frac{\sqrt{3}}{2}e^{-i\hat{H}t/\hbar}|\psi_1\rangle \tag{2}$$
$$= \frac{1}{2}e^{-iE_0t/\hbar}|\psi_0\rangle + \frac{\sqrt{3}}{2}e^{-iE_1t/\hbar}|\psi_1\rangle \tag{3}$$

(b)

$$P_g(t) = |\langle\psi_0|\psi(t)\rangle|^2 = \frac{1}{4} \tag{4}$$

(c)

$$\langle E\rangle = \langle\psi(t)|\hat{H}|\psi(t)\rangle \tag{5}$$
$$= \frac{1}{4}\langle\psi_0|\hat{H}|\psi_0\rangle + \frac{3}{4}\langle\psi_1|\hat{H}|\psi_1\rangle + \frac{\sqrt{3}}{2}\mathrm{Re}[\langle\psi_0|\hat{H}|\psi_1\rangle e^{-i(E_1-E_0)t/\hbar}] \tag{6}$$
$$= \frac{1}{4}E_0 + \frac{3}{4}E_1 \tag{7}$$

(d)

$$\langle q\rangle = \langle\psi(t)|\hat{q}|\psi(t)\rangle \tag{8}$$
$$= \frac{1}{4}\langle\psi_0|\hat{q}|\psi_0\rangle + \frac{3}{4}\langle\psi_1|\hat{q}|\psi_1\rangle + \frac{\sqrt{3}}{2}\mathrm{Re}[\langle\psi_0|\hat{q}|\psi_1\rangle e^{-i(E_1-E_0)t/\hbar}] \tag{9}$$

The bond length and electric dipole will, in general, depend on time because the last term is not necessarily zero.

Problem 2: Commutator

(a)

$$
\begin{aligned}
[B, A] &= BA - AB = -(AB - BA) = -[A, B] \\
[\lambda A, B] &= \lambda AB - B\lambda A = \lambda(AB - BA) = \lambda [A, B] \\
[A, B + C] &= A(B + C) - (B + C)A \\
&= AB + AC - BA - CA \\
&= AB - BA + AC - AC \\
&= [A, B] + [A, C] \\
[A, [B, C]] + [B, [C, A]] + [C, [A, B]] &= [A, (BC - CB)] + [B, (CA - AC)] + [C, (AB - BA)] \\
&= ABC - ACB - BCA + CBA + BCA - BAC - CAB \\
&\qquad + ACB + CAB - CBA - ABC + BAC \\
&= 0
\end{aligned}
$$

(b)

$$
\begin{aligned}
[A, BC] &= ABC - BCA \\
&= ABC - BAC + BAC - BCA \\
&= (AB - BA)C + B(AC - CA) \\
&= B [A, C] + [A, B] C
\end{aligned}
$$

(c) From the question, we know that $g(p) = \sum_{n=0}^{\infty} a_n p^n$, where we set the center of the series to be 0 without loss of generality and where $a_n = g^{(n)}(0)/n!$. Therefore, we have

$$
[q, g(p)] = [q, \sum_{n=0}^{\infty} a_n p^n] = \sum_{n=0}^{\infty} a_n [q, p^n] \tag{10}
$$

by using the bilinearity of commutators. Hence, we need to find what $[q, p^n]$ is to find what $[q, g(p)]$ is.

We shall now use the claim of the exercise

$$
[q, g(p)] = i\hbar \frac{dg}{dp} \tag{11}
$$

with $g(p) = p^n$ in order to devise the hypothesis that

$$
[q, p^n] = i\hbar \frac{d}{dp} p^n = ni\hbar p^{n-1}. \tag{12}
$$

Let us now prove the hypothesis, $[q, p^n] = ni\hbar p^{n-1}$, by induction:

1) Base case:

$$
[q, p] = i\hbar = i\hbar p^0.
$$

2) Induction step:

$$
\begin{aligned}
[q, p^n] &= p[q, p^{n-1}] + [q, p]p^{n-1} && \text{(Leibnitz rule)} \\
&= (n - 1)i\hbar p p^{n-2} + i\hbar p^{n-1} && \text{(Used induction hypothesis)} \\
&= ni\hbar p^{n-1}.
\end{aligned} \tag{13}
$$

Now substituting the result of Eq. (13) into Eq. (10), we obtain

$$
[q, g(p)] = i\hbar \sum_{n=0}^{\infty} n a_n p^{n-1} = i\hbar \frac{dg}{dp}. \tag{14}
$$

$[p, f(q)] = -i\hbar f'(q)$ follows analogously by recognizing that $[p, q] = -[q, p] = -i\hbar$.