Molecular quantum dynamics: Solutions 4

Problem 1: Energy of a coherent state

Note that $-i\alpha_t = -i\alpha_0 = m\omega > 0$ and $H(q_t, p_t) = \frac{p_t^2}{2m} + \frac{1}{2}m\omega^2 q_t^2$.
Prerequisites:

$$\int |\psi(x,t)|^2 dx = 1$$

$$\int (x - q_t)|\psi(x,t)|^2 dx = 0,$$

$$\int (x - q_t)^2|\psi(x,t)|^2 dx = \frac{\hbar}{2m\omega},$$

$$\begin{aligned}
\frac{\partial^2}{\partial x^2}\psi(x,t) &= \left\{-\frac{1}{\hbar^2}\left[\alpha_0(x-q_t)+p_t\right]^2 + \frac{i}{\hbar}\alpha_t\right\}\psi(x,t) \\
&= \left\{-\frac{1}{\hbar^2}\left[\alpha_0^2(x-q_t)^2 + 2\alpha_0 p_t(x-q_t) + p_t^2\right] + \frac{i}{\hbar}\alpha_0\right\}\psi(x,t) \\
x^2\psi(x,t) &= \left\{(x-q_t)^2 + 2q_t(x-q_t) + q_t^2\right\}\psi(x,t).
\end{aligned}$$

$$\begin{aligned}
E(t) &= \langle\psi(t)|\hat{H}|\psi(t)\rangle \\
&= \int \psi(x,t)^* \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + \frac{1}{2}m\omega^2 x^2\psi(x,t)\right] dx \\
&= \int \psi(x,t)^* \Bigg[\frac{1}{2}\left(m\omega^2 + \frac{\alpha_0^2}{m}\right)(x-q_t)^2 + \left(\frac{\alpha_0 p_t}{m} + m\omega^2 q_t\right)(x-q_t) \\
&\qquad\qquad + \frac{p_t^2}{2m} - \frac{i\hbar}{2m}\alpha_0 + \frac{1}{2}m\omega^2 q_t^2\Bigg]\psi(x,t)dx \\
&= \frac{1}{2}\left(m\omega^2 + \frac{\alpha_0^2}{m}\right)\int (x-q_t)^2|\psi(x,t)|^2 dx + \left(\frac{\alpha_0 p_t}{m} + m\omega^2 q_t\right)\int (x-q_t)|\psi(x,t)|^2 dx \\
&\qquad\qquad + \left(\frac{p_t^2}{2m} - \frac{i\hbar}{2m}\alpha_0 + \frac{1}{2}m\omega^2 q_t^2\right)\int |\psi(x,t)|^2 dx \\
&= \frac{\hbar}{4m\omega}\left(m\omega^2 + \frac{\alpha_0^2}{m}\right) - \frac{i\hbar}{2m}\alpha_0 + \frac{p_t^2}{2m} + \frac{1}{2}m\omega^2 q_t^2 \\
&= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} + \frac{p_t^2}{2m} + \frac{1}{2}m\omega^2 q_t^2 \\
&= H(q_t, p_t) + \frac{\hbar\omega}{2}
\end{aligned}$$

Problem 2: Lagrangian and Hamiltonian for a diatomic molecule (or the hydrogen atom)

a) We first invert

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$
$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{M}$$

to obtain

$$\mathbf{r}_1 = \mathbf{R} - \frac{m_2}{M}\mathbf{r}$$
$$\mathbf{r}_2 = \mathbf{R} + \frac{m_1}{M}\mathbf{r}.$$

Then, we substitute $\mathbf{r}_1$ and $\mathbf{r}_2$ in the expression for the kinetic energy:

$$\begin{aligned}
T &= \frac{1}{2}m_1\dot{\mathbf{r}}_1^2 + \frac{1}{2}m_2\dot{\mathbf{r}}_2^2 \\
&= \frac{1}{2}m_1(\dot{\mathbf{R}} - \frac{m_2}{M}\dot{\mathbf{r}})^2 + \frac{1}{2}m_2(\dot{\mathbf{R}} + \frac{m_1}{M}\dot{\mathbf{r}})^2 \\
&= \frac{1}{2}(m_1 + m_2)\dot{\mathbf{R}}^2 + \frac{1}{2}(\frac{m_1 m_2^2}{M^2} + \frac{m_2 m_1^2}{M^2})\dot{\mathbf{r}}^2 \\
&= \frac{1}{2}M\dot{\mathbf{R}}^2 + \frac{1}{2}\mu\dot{\mathbf{r}}^2
\end{aligned}$$

and the Lagrangian is

$$L(\mathbf{r}, \dot{\mathbf{r}}, \dot{\mathbf{R}}) = \frac{1}{2}M\dot{\mathbf{R}}^2 + \frac{1}{2}\mu\dot{\mathbf{r}}^2 - V(\mathbf{r}).$$

b) For $\mathbf{r}$ we have

$$\begin{aligned}
\frac{\partial L}{\partial \mathbf{r}} - \frac{d}{dt}\frac{\partial L}{\partial \dot{\mathbf{r}}} &= 0 \\
-\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}} - \mu\ddot{\mathbf{r}} &= 0 \\
\mu\ddot{\mathbf{r}} &= -\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}}
\end{aligned}$$

For $\mathbf{R}$ we have

$$\begin{aligned}
\frac{\partial L}{\partial \mathbf{R}} - \frac{d}{dt}\frac{\partial L}{\partial \dot{\mathbf{R}}} &= 0 \\
0 - M\ddot{\mathbf{R}} &= 0 \\
M\ddot{\mathbf{R}} &= 0
\end{aligned}$$

Solution for $\mathbf{R}$:

$$\mathbf{R}(t) = \mathbf{R}_0 + \dot{\mathbf{R}}_0 t,$$

which corresponds to a uniform motion, i.e., the velocity $\dot{\mathbf{R}}_0$ is constant, as it should be for the center of mass of a two-body system, where the interaction between the two particles is given by the central potential $V(\mathbf{r})$.

c) Momenta are

$$\mathbf{p} := \frac{\partial L}{\partial \dot{\mathbf{r}}} = \mu\dot{\mathbf{r}}$$
$$\mathbf{P} := \frac{\partial L}{\partial \dot{\mathbf{R}}} = M\dot{\mathbf{R}}$$

d) Hamiltonian is

$$\begin{aligned} H(\mathbf{r}, \mathbf{R}, \mathbf{p}, \mathbf{P}) &= \dot{\mathbf{r}}\mathbf{p} + \dot{\mathbf{R}}\mathbf{P} - L(\mathbf{r}, \dot{\mathbf{r}}, \dot{\mathbf{R}}) \\ &= \frac{\mathbf{p}^2}{\mu} + \frac{\mathbf{P}^2}{M} - \left[\frac{\mathbf{p}^2}{2\mu} + \frac{\mathbf{P}^2}{2M} - V(\mathbf{r})\right] \\ &= \frac{\mathbf{p}^2}{2\mu} + \frac{\mathbf{P}^2}{2M} + V(\mathbf{r}) \end{aligned}$$

e) For $\mathbf{r}$:

$$\begin{aligned} \dot{\mathbf{p}} &= -\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}} \\ \dot{\mathbf{r}} &= \frac{\partial H}{\partial \mathbf{p}} = \frac{\mathbf{p}}{\mu} \end{aligned}$$

For $\mathbf{R}$:

$$\begin{aligned} \dot{\mathbf{P}} &= -\frac{\partial H}{\partial \mathbf{R}} = 0 \\ \dot{\mathbf{R}} &= \frac{\partial H}{\partial \mathbf{P}} = \frac{\mathbf{P}}{M} \end{aligned}$$

Solving for $\mathbf{R}$ gives

$$\begin{aligned} \mathbf{P}(t) &= \mathbf{P}_0 \\ \mathbf{R}(t) &= \mathbf{R}_0 + \frac{\mathbf{P}_0}{M} t. \end{aligned}$$