Molecular quantum dynamics: Exercise series 4

Problem 1: Energy of a coherent state

Consider the coherent state of the harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2,$$

i.e., a Gaussian wavepacket

$$\psi(x,t) = N \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\alpha_t\left(x-q_t\right)^2 + p_t(x-q_t) + \gamma_t\right]\right\}$$

with a constant width parameter $\alpha_t = \alpha_0 = im\omega$. Show that the expectation value of energy in the state $\psi(t)$ satisfies

$$E(t) := \langle\psi(t)|\hat{H}|\psi(t)\rangle = H(q_t,p_t) + c\hbar\omega$$

and find the constant c. Note: $H(q_t,p_t)$ is the *classical* energy of the center of the wavepacket!

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

Consider a two-body problem, i.e., two particles of mass m_1 and m_2 interacting via a potential energy depending only on the distance, $V(\mathbf{r}_1,\mathbf{r}_2) = V(|\mathbf{r}_2-\mathbf{r}_1|)$. An example is a diatomic molecule in the Born-Oppenheimer approximation, where the two particles are two nuclei and V is the Born-Oppenheimer potential energy surface. Another example is the hydrogen atom, where the two particles are the proton and electron, $m_1 = m_p$ and $m_2 = m_e$, and $V = -\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_2-\mathbf{r}_1|}$ is the Coulomb interaction. Because the potential energy depends only on the distance of the two particles, it is convenient to use new coordinates $\mathbf{r} := \mathbf{r}_2 - \mathbf{r}_1$ (the relative coordinate) and $\mathbf{R} := \frac{m_1\mathbf{r}_1+m_2\mathbf{r}_2}{m_1+m_2}$ (the *center-of-mass* coordinate). This is the simplest example of so-called *Jacobi coordinates*.

a) Kinetic energy in the original coordinates is $T = \frac{1}{2}m_1\dot{\mathbf{r}}_1^2 + \frac{1}{2}m_2\dot{\mathbf{r}}_2^2$. Express the kinetic energy in coordinates $\dot{\mathbf{r}}$ and $\dot{\mathbf{R}}$. Simplify the result by using the total mass $M := m_1 + m_2$ and the *reduced mass* $\mu := \frac{m_1m_2}{m_1+m_2}$. Express the Lagrangian L in coordinates $\mathbf{r}, \mathbf{R}, \dot{\mathbf{r}}$, and $\dot{\mathbf{R}}$.

b) Write down the Lagrange equations of motion for $\mathbf{r}$ and $\mathbf{R}$. Solve the equation for the center of mass $\mathbf{R}$. Does it correspond to your intuition? (Equation for $\mathbf{r}$ will be solved in the lecture.)

c) Using the definition from class, what are the momenta $\mathbf{p}$ and $\mathbf{P}$ conjugate to the coordinates $\mathbf{r}$ and $\mathbf{R}$? (Express them in terms of $\dot{\mathbf{r}}$ and $\dot{\mathbf{R}}$.)

d) Write down the Hamiltonian $H(\mathbf{r},\mathbf{R},\mathbf{p},\mathbf{P})$.

e) Write down Hamilton's equations of motion for $\mathbf{r}, \mathbf{R}, \mathbf{p}$, and $\mathbf{P}$. Solve the equations for $\mathbf{R}$ and $\mathbf{P}$; the solution should agree with part b). (Equations for $\mathbf{r}$ and $\mathbf{p}$ will be solved in the lecture.)

Note: In this homework, you have separated the center-of-mass motion from the relative motion. In the next lecture we will study the relative motion. In hydrogen atom, the reduced mass $\mu \approx m_e$ since proton is much heavier than the electron, and in many texts this approximation is used and the center-of-mass motion is forgotten from the beginning. In more accurate calculations, one has to consider μ instead of m_e.