Molecular quantum dynamics: Solutions 3

Problem 1: Ion in a uniform electric field

As we shall see, the solution of the time-dependent Schrödinger equation $i\hbar d\psi(t)/dt = [T(\hat{p}) + V(\hat{q})]\psi(t)$ with a potential energy function $V(q)$ that is linear in position q is a Gaussian wavepacket,

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

at all times t if the initial state is also a Gaussian wavepacket. Therefore, we will use the Gaussian wavepacket as an ansatz.
The time-dependent Schrödinger equation in the q-representation is given as

$$i\hbar\frac{\partial\psi(q,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + V(q)\right]\psi(q,t). \tag{2}$$

The required partial derivatives of Eq. (1) are

$$\frac{\partial\psi}{\partial t} = \frac{i}{\hbar}\left[\frac{1}{2}\dot{\alpha}_t(q-q_t)^2 + (\dot{p}_t - \alpha_t\dot{q}_t)(q-q_t) - \dot{q}_t p_t + \dot{\gamma}_t\right]\psi, \tag{3}$$

$$\frac{\partial^2\psi}{\partial q^2} = \left\{\left(\frac{i}{\hbar}\right)^2[\alpha_t(q-q_t)+p_t]^2 + \frac{i}{\hbar}\alpha_t\right\}\psi. \tag{4}$$

Substitution of these in Eq. (2) with $V(q) = -QEq$ yields

$$\begin{aligned}&-\left[\frac{1}{2}\dot{\alpha}_t(q-q_t)^2 + (\dot{p}_t - \alpha_t\dot{q}_t)(q-q_t) - \dot{q}_t p_t + \dot{\gamma}_t\right]\\ &= \frac{\alpha_t^2}{2m}(q-q_t)^2 + \left(\frac{\alpha_t p_t}{m} - QE\right)(q-q_t) + \frac{p_t^2}{2m} - QEq_t - \frac{i\hbar\alpha_t}{2m}.\end{aligned} \tag{5}$$

Equation (5) has to hold for all q. Collecting terms of the same order in $(q-q_t)$ gives us the following three equations.

$$(q-q_t)^2: \qquad \frac{1}{2}(\dot{\alpha}_t + \alpha_t^2/m) = 0 \tag{6}$$

$$(q-q_t)^1: \qquad \alpha_t\dot{q}_t - \dot{p}_t = \alpha_t\frac{p_t}{m} - QE \tag{7}$$

$$(q-q_t)^0: \qquad \dot{\gamma}_t = -\frac{p_t^2}{2m} + p_t\dot{q}_t + QEq_t + \frac{i\hbar}{2m}\alpha_t \tag{8}$$

We first solve Eq. (6):

$$\alpha_t^{-2}\frac{d\alpha_t}{dt} = -m^{-1} \tag{9}$$

$$\int_{\alpha_0}^{\alpha_t}\alpha^{-2}d\alpha = -\int_0^t m^{-1}d\tau \tag{10}$$

$$-\alpha_t^{-1} + \alpha_0^{-1} = -t/m \tag{11}$$

$$\alpha_t = \frac{m\alpha_0}{m+\alpha_0 t} \tag{12}$$

Next we solve Eq. (7). We first use that the position q_t and the momentum p_t are real, i.e. $\mathrm{Im}(q_t) = \mathrm{Im}(p_t) = 0$ and take the imaginary part of Eq. (7):

$$\mathrm{Im}(\alpha_t)\dot{q}_t = \mathrm{Im}(\alpha_t)\frac{p_t}{m} \tag{13}$$

$$\dot{q}_t = \frac{p_t}{m}, \tag{14}$$

where we used the fact that $\mathrm{Im}(\alpha_t) > 0$ in a Gaussian wavepacket.
Substituting Eq. (14) back into Eq. (7) yields

$$\dot{p}_t = QE. \tag{15}$$

We solve Eq. (15) to obtain $p_t = p_0 + QEt$, then substitute this into Eq. (14) and solve for q_t:

$$\dot{q}_t = \frac{1}{m}(p_0 + QEt) \tag{16}$$

$$q_t = q_0 + \frac{p_0 t}{m} + \frac{QEt^2}{2m}. \tag{17}$$

Finally, let us substitute Eq. (14) into Eq. (8) to obtain

$$\dot{\gamma}_t = L_{\mathrm{cl}} + \frac{i\hbar}{2m}\alpha_t \tag{18}$$

with

$$\begin{aligned} L_{\mathrm{cl}} &= \frac{p_t^2}{2m} + QEq_t \\ &= \frac{p_0^2}{2m} + QEq_0 + \frac{2QEp_0 t}{m} + \frac{Q^2E^2t^2}{m}. \end{aligned} \tag{19}$$

Integrating Eq. (18) gives

$$\int_{\gamma_0}^{\gamma_t} d\gamma = \int_0^t L_{\mathrm{cl}} d\tau + \frac{i\hbar}{2m}\int_0^t \alpha_\tau d\tau \tag{20}$$

$$\gamma_t = \gamma_0 + \int_0^t L_{\mathrm{cl}} d\tau + \frac{i\hbar}{2m}\int_0^t \alpha_\tau d\tau. \tag{21}$$

We note that

$$\alpha_t = m\frac{\dot{z}}{z} = m\frac{d}{dt}\log(z) \tag{22}$$

with $z(t) = m + \alpha_0 t$ to obtain

$$\int_0^t \alpha_\tau d\tau = m\log[z(t)/z(0)] = m\log(1 + \alpha_0 t/m). \tag{23}$$

Noting that L_{cl} in Eq. (19) is a quadratic function of t, we finally get

$$\gamma_t = \gamma_0 + \left(\frac{p_0^2}{2m} + QEq_0\right)t + \frac{QEp_0t^2}{m} + \frac{Q^2E^2t^3}{3m} + \frac{i\hbar}{2}\log\left(1 + \frac{\alpha_0 t}{m}\right). \tag{24}$$