Molecular quantum dynamics: Solutions 10

Fourier method for a molecule in magnetic field:

a) The Hamiltonian can be written as

$$\hat{H} = \frac{1}{2m}(\hat{p} - A(\hat{q}))^2 \tag{1}$$

$$= \frac{1}{2m}\left[\hat{p}^2 - \hat{p}\,A(\hat{q}) - A(\hat{q})\,\hat{p} + A^2(\hat{q})\right], \tag{2}$$

where hat $\hat{}$ denotes a general operator and the **bold** font used to denote a D-dimensional vector in the nuclear degrees of freedom has been omitted for simplicity. We cannot apply split-operator method for this Hamiltonian because we cannot divide $\hat{p}\,A(\hat{q})$ and $A(\hat{q})\,\hat{p}$ into a sum of several terms which depend either only on $\hat{q}$ or $\hat{p}$. Split-operator is only applicable to Hamiltonians that can be separated into terms depending purely on either the position $\hat{q}$ or momentum $\hat{p}$ operator.
b) Fourier Method reads

$$|\psi(t+\Delta t)\rangle = |\psi(t)\rangle - \frac{i}{\hbar}\Delta t \hat{H}|\psi(t)\rangle. \tag{3}$$

Therefore, in order to find $\psi(q, t+\Delta t) := \langle q|\psi(t+\Delta t)\rangle$, we have to evaluate $\langle q|\hat{H}|\psi(t)\rangle$, which is composed of four terms:

1. $\langle q|\hat{p}^2|\psi(t)\rangle$
2. $\langle q|\hat{p}\,A(\hat{q})|\psi(t)\rangle$
3. $\langle q|A(\hat{q})\,\hat{p}|\psi(t)\rangle$
4. $\langle q|A^2(\hat{q})|\psi(t)\rangle$

The goal is to evaluate each one of these expressions by performing the appropriate changes of the representation.
First one is

$$\langle q|\hat{p}^2|\psi(t)\rangle = \int_{-\infty}^{\infty} dp \langle q|\hat{p}^2|p\rangle\langle p|\psi(t)\rangle \tag{4}$$

$$= \int_{-\infty}^{\infty} dp \langle q|p\rangle p^2 \tilde{\psi}(p,t) \tag{5}$$

$$= \int_{-\infty}^{\infty} dp \frac{1}{\sqrt{2\pi\hbar}} e^{iqp/\hbar}\, p^2\, \tilde{\psi}(p,t) \tag{6}$$

So the recipe for the first term is similar to what was done in the class:

1. Fourier transformation (change the representation from the position to the momentum representation)

2. Multiply with p^2 in the momentum representation

3. Inverse Fourier transformation (change back to the position representation)

Second term is given by

$$\begin{aligned}
\langle q|\hat{p}\, A(\hat{q})|\psi(t)\rangle &= \int_{-\infty}^{\infty} dq' \langle q|\hat{p}\, A(\hat{q})|q'\rangle\langle q'|\psi(t)\rangle && (7)\\
&= \int_{-\infty}^{\infty} dq' \langle q|\hat{p}|q'\rangle\, A(q')\, \psi(q',t) && (8)\\
&= \int_{-\infty}^{\infty} dq' \int_{-\infty}^{\infty} dp \langle q|\hat{p}|p\rangle\, \langle p|q'\rangle\, A(q')\, \psi(q',t) && (9)\\
&= \int_{-\infty}^{\infty} dq' \int_{-\infty}^{\infty} dp \langle q|p\rangle p\, \frac{1}{\sqrt{2\pi\hbar}} e^{-iq'p/\hbar}\, A(q')\, \psi(q',t) && (10)\\
&= \int_{-\infty}^{\infty} dq' \int_{-\infty}^{\infty} dp \frac{1}{\sqrt{2\pi\hbar}} e^{iqp/\hbar} p\, \frac{1}{\sqrt{2\pi\hbar}} e^{-iq'p/\hbar}\, A(q')\, \psi(q',t) && (11)\\
&= \int_{-\infty}^{\infty} dp \frac{1}{\sqrt{2\pi\hbar}} e^{iqp/\hbar} p \int_{-\infty}^{\infty} dq' \frac{1}{\sqrt{2\pi\hbar}} e^{-iq'p/\hbar}\, A(q')\, \psi(q',t) && (12)
\end{aligned}$$

The algorithm to evaluate this term is:

1. Multiply with $A(q)$ in the position representation

2. Fourier transform the product $A(q)\psi(q,t)$(change representation from the position to the momentum representation)

3. Multiply with p in the momentum representation

4. Inverse Fourier transformation (change back to position representation)

Third term we express as

$$\begin{aligned}
\langle q|A(\hat{q})\, \hat{p}|\psi(t)\rangle &= \int_{-\infty}^{\infty} dp \langle q|A(\hat{q})\, \hat{p}|p\rangle\langle p|\psi(t)\rangle && (13)\\
&= \int_{-\infty}^{\infty} dp A(q)\langle q|p\rangle p\langle p|\psi(t)\rangle && (14)\\
&= A(q) \int_{-\infty}^{\infty} dp \frac{1}{\sqrt{2\pi\hbar}} e^{iqp/\hbar} p\tilde{\psi}(p,t) && (15)
\end{aligned}$$

The algorithm is

1. Fourier transform (change representation from the position to the momentum representation)

2. Multiply with p in the momentum representation

3. Inverse Fourier transformation (change back to the position representation)

4. Multiply with $A(q)$ in the position representation

Finally, fourth term is the simplest as it is just multiplication in the position representation

$$\begin{aligned}
\langle q|A^2(\hat{q})|\psi(t)\rangle &= A^2(q)\, \langle q|\psi(t)\rangle && (16)\\
&= A^2(q)\, \psi(q,t) && (17)
\end{aligned}$$

Of course, the most efficient algorithm does not evaluate the common steps more than once. For example, the state at time t in the momentum representation is required both for evaluating the first and the third term in the Hamiltonian, so it will be computed only once for both terms. Nevertheless, the algorithm involves more steps and more transformations than in the case of simple separable Hamiltonian that can be split into a kinetic term that only depends on the momentum operator and a potential term that only depends on the position operator.