Molecular quantum dynamics: Solutions 6

Problem 1: Properties of the Wigner function

Wigner function $\rho_W(q,p)$ of a wavefunction $\psi(q)$ is

$$\rho_W(q,p) := \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \psi\left(q-\frac{s}{2}\right)\psi^*\left(q+\frac{s}{2}\right)e^{ips/\hbar}ds.$$

We will use the following properties:

(1) $\int e^{ipq/\hbar}dq = 2\pi\hbar\delta(p)$

(2) $\int dx f(x,y)\delta(x) = f(0,y)$

(3) $\tilde{\psi}(p) = \langle p|\psi\rangle = (2\pi\hbar)^{-1/2}\int_{-\infty}^{\infty}\psi(q)e^{-iqp/\hbar}dq$

(4) $\int dp|p\rangle\langle p| = 1$

(5) $\langle q|p\rangle = (2\pi\hbar)^{-1/2}e^{iqp/\hbar}$

(6) $\delta(aq) = \frac{1}{|a|}\delta(q)$

(7) $\int dx f(x)\delta(y-x) = f(y)$

(a)

$$\begin{aligned}
\int \rho_W(q,p)dp &= \frac{1}{2\pi\hbar}\int ds\langle q-\frac{s}{2}|\psi\rangle\langle\psi|q+\frac{s}{2}\rangle\int dp e^{ips/\hbar} \\
&\overset{(1)}{=} \frac{1}{2\pi\hbar}\int ds\langle q-\frac{s}{2}|\psi\rangle\langle\psi|q+\frac{s}{2}\rangle 2\pi\hbar\delta(s) \\
&\overset{(2)}{=} \langle q|\psi\rangle\langle\psi|q\rangle = |\psi(q)|^2
\end{aligned}$$

(b)

$$\begin{aligned}
\int \rho_W(q,p)dq &= \frac{1}{2\pi\hbar}\int dq\int ds\langle\psi|q+\frac{s}{2}\rangle\langle q-\frac{s}{2}|\psi\rangle e^{ips/\hbar} \\
&\overset{\text{hint, (4)}}{=} \frac{1}{2\pi\hbar}\int dq\int ds\int dp_1\int dp_2\langle\psi|p_1\rangle\langle p_1|q+\frac{s}{2}\rangle\langle q-\frac{s}{2}|p_2\rangle\langle p_2|\psi\rangle e^{ips/\hbar} \\
&\overset{(3),(5)}{=} \frac{1}{(2\pi\hbar)^2}\int dq\int ds\int dp_1\int dp_2 e^{-ip_1(q+s/2)/\hbar}e^{ip_2(q-s/2)/\hbar}\tilde{\psi}^*(p_1)\tilde{\psi}(p_2)e^{ips/\hbar} \\
&= \frac{1}{(2\pi\hbar)^2}\int dq\int ds\int dp_1\int dp_2\tilde{\psi}^*(p_1)\tilde{\psi}(p_2)\exp\left[\frac{i}{\hbar}s\left(-\frac{p_1}{2}-\frac{p_2}{2}+p\right)\right]\exp\left[\frac{i}{\hbar}q\left(p_2-p_1\right)\right]
\end{aligned}$$

Now, we can either integrate first over s or integrate first over q—both approaches give the correct result. If we integrate first over q, we have

$$\begin{aligned}
\int \rho_W(q,p)dq &\overset{(1)}{=} \frac{1}{2\pi\hbar}\int ds \int dp_1 \int dp_2 \tilde{\psi}^*(p_1)\tilde{\psi}(p_2)\exp\left[\frac{i}{\hbar}s\left(-\frac{p_1}{2}-\frac{p_2}{2}+p\right)\right]\delta(p_2-p_1) \\
&\overset{(7)}{=} \frac{1}{2\pi\hbar}\int ds \int dp_1 \tilde{\psi}^*(p_1)\tilde{\psi}(p_1)\exp\left[\frac{i}{\hbar}s\left(p-p_1\right)\right] \\
&\overset{(1)}{=} \int dp_1 \tilde{\psi}^*(p_1)\tilde{\psi}(p_1)\delta\left(p-p_1\right) = |\tilde{\psi}(p)|^2
\end{aligned}$$

If we integrate first over s:

$$\begin{aligned}
\int \rho_W(q,p)dq &\overset{(1)}{=} \frac{1}{2\pi\hbar}\int dq \int dp_1 \int dp_2 \tilde{\psi}^*(p_1)\tilde{\psi}(p_2)\delta\left(p-\frac{p_2}{2}-\frac{p_1}{2}\right)\exp\left[\frac{i}{\hbar}q\left(p_2-p_1\right)\right] \\
&\overset{(6),(7)}{=} \frac{1}{\pi\hbar}\int dq \int dp_1 \tilde{\psi}^*(p_1)\tilde{\psi}(2p-p_1)\exp\left[\frac{i}{\hbar}q\left(2p-2p_1\right)\right] \\
&\overset{(1)}{=} 2\int dp_1 \tilde{\psi}^*(p_1)\tilde{\psi}(2p-p_1)\delta(2p-2p_1) \\
&\overset{(6),(7)}{=} \tilde{\psi}^*(p)\tilde{\psi}(2p-p) = |\tilde{\psi}(p)|^2
\end{aligned}$$

Alternative solution to (b)

$$\int \rho_w(q,p)dq = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dq ds \psi(q-s/2)\psi^*(q+s/2)e^{ips/\hbar}$$

can be solved by changing the variables to $x = q - s/2$ and $y = q + s/2$. Noting that

$$\begin{vmatrix} \frac{\partial q}{\partial x} & \frac{\partial q}{\partial y} \\ \frac{\partial s}{\partial x} & \frac{\partial s}{\partial y} \end{vmatrix} = \begin{vmatrix} \frac{1}{2} & \frac{1}{2} \\ -1 & 1 \end{vmatrix} = 1,$$

we obtain

$$\begin{aligned}
\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dq ds \psi(q-s/2)\psi^*(q+s/2)e^{ips/\hbar} &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx dy \psi(x)\psi^*(y)e^{ip(y-x)/\hbar} \\
&= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(x)e^{-ipx/\hbar}dx \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi^*(y)e^{ipy/\hbar}dy \\
&= \tilde{\psi}(p)\tilde{\psi}(p)^* \\
&= |\tilde{\psi}(p)|^2.
\end{aligned}$$