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Some integrals with Gaussian wavepackets

1. Definition

The normalized Gaussian wavepacket is defined as:

$$G = \left(\frac{a}{\pi}\right)^{1/4} \exp\left(-\frac{a}{2}(x - x_0)^2 + ip_0(x - x_0)\right). \qquad (1)$$

Here, a is the width parameter, x_0 is the center of wavepacket, p_0 is the momentum of wavepacket.

2. Overlap integral

$$\begin{aligned}
S_{12} &= \int G_1^* G_2 dx = \left(\frac{a}{\pi}\right)^{1/2} \int \exp\left(-\frac{a}{2}(x - x_{0,1})^2 - \frac{a}{2}(x - x_{0,2})^2 - ip_{0,1}(x - x_{0,1}) + ip_{0,2}(x - x_{0,2})\right) dx = \\
&= \left(\frac{a}{\pi}\right)^{1/2} \int \exp\left(\left[-ax^2 + a(x_{0,1} + x_{0,2})x - \frac{a}{2}(x_{0,1}^2 + x_{0,2}^2) + i(p_{0,1}x_{0,1} - p_{0,2}x_{0,2})\right] + ix(p_{0,2} - p_{0,1})\right) dx = \\
&= \left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}(x_{0,1}^2 + x_{0,2}^2) + i(p_{0,1}x_{0,1} - p_{0,2}x_{0,2})\right) \int \exp\left(-ax^2 + [a(x_{0,1} + x_{0,2}) + i(p_{0,2} - p_{0,1})]x\right) dx = \\
&= \exp\left(-\frac{a}{2}(x_{0,1}^2 + x_{0,2}^2) + i(p_{0,1}x_{0,1} - p_{0,2}x_{0,2})\right) \exp\left(\frac{[a(x_{0,1} + x_{0,2}) + i(p_{0,2} - p_{0,1})]^2}{4a}\right) = \\
&= \exp\left(-\frac{a}{4}(x_{0,1} - x_{0,2})^2 - \frac{1}{4a}(p_{0,2} - p_{0,1})^2\right) \exp\left(i\left((x_{0,1} - x_{0,2})\frac{(p_{0,1} + p_{0,2})}{2}\right)\right)
\end{aligned} \qquad (2)$$

Here, we have used the integral

$$\int \exp(-ax^2 + bx + c) dx = \left(\frac{\pi}{a}\right)^{1/2} \exp\left(\frac{b^2}{4a} + c\right) \qquad (3)$$

3. Position expectation value

$$\begin{aligned}
\mu_{12} &= \int G_1^* x G_2 dx = \left(\frac{a}{\pi}\right)^{1/2} \int x \exp\left(-\frac{a}{2}(x - x_{0,1})^2 - \frac{a}{2}(x - x_{0,2})^2 - ip_{0,1}(x - x_{0,1}) + ip_{0,2}(x - x_{0,2})\right) dx = \\
&= \left(\frac{a}{\pi}\right)^{1/2} \int x \exp\left(\left[-ax^2 + a(x_{0,1} + x_{0,2})x - \frac{a}{2}(x_{0,1}^2 + x_{0,2}^2) + i(p_{0,1}x_{0,1} - p_{0,2}x_{0,2})\right] + ix(p_{0,2} - p_{0,1})\right) dx = \\
&= \left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}(x_{0,1}^2 + x_{0,2}^2) + i(p_{0,1}x_{0,1} - p_{0,2}x_{0,2})\right) \int x \exp\left(-ax^2 + [a(x_{0,1} + x_{0,2}) + i(p_{0,2} - p_{0,1})]x\right) dx = \\
&= \\
&= \left(\frac{b}{2a}\right) \exp\left(-\frac{a}{2}(x_{0,1}^2 + x_{0,2}^2) + i(p_{0,1}x_{0,1} - p_{0,2}x_{0,2})\right) \exp\left(\frac{[a(x_{0,1} + x_{0,2}) + i(p_{0,2} - p_{0,1})]^2}{4a}\right) = \\
&= \left(\frac{b}{2a}\right) S_{12} = \frac{a(x_{0,1} + x_{0,2}) + i(p_{0,2} - p_{0,1})}{2a} S_{12} = \left[\frac{(x_{0,1} + x_{0,2})}{2} + i\frac{(p_{0,2} - p_{0,1})}{2a}\right] S_{12}
\end{aligned}$$

$$\int x \exp\left(-ax^2 + bx + c\right)dx = \int x \exp\left(-a\left(x^2 - 2\frac{b}{2a}x + \left(\frac{b}{2a}\right)^2 - \left(\frac{b}{2a}\right)^2\right) + c\right)dx =$$
$$= \int x \exp\left(-a\left(x - \frac{b}{2a}\right)^2 + \left(\frac{b^2}{4a} + c\right)\right)dx = \exp\left(\frac{b^2}{4a} + c\right)\int x \exp\left(-a\left(x - \frac{b}{2a}\right)^2\right)dx =$$
$$= \left| y = x - \frac{b}{2a}, dx = dy \right| = \exp\left(\frac{b^2}{4a} + c\right)\int\left(y + \frac{b}{2a}\right)\exp\left(-ay^2\right)dy =$$
$$= \exp\left(\frac{b^2}{4a} + c\right)\left[\frac{b}{2a}\left(\frac{\pi}{a}\right)^{1/2}\right]$$

4. Derivative coupling integral

$$\begin{aligned} D_{12} &= \int G_1^* \nabla G_2 dx = \left(\frac{a}{\pi}\right)^{1/2} \int \left[-a\left(x - x_{0,2}\right) + ip_{0,2}\right] \exp\left(-\frac{a}{2}\left(x - x_{0,1}\right)^2 - \frac{a}{2}\left(x - x_{0,2}\right)^2 - ip_{0,1}\left(x - x_{0,1}\right) + ip_{0,2}\left(x - x_{0,2}\right)\right)dx = \\ &= \left(ax_{0,2} + ip_{0,2}\right)S - a\left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right)\right)\int x \exp\left(-ax^2 + \left[a\left(x_{0,1} + x_{0,2}\right) + i\left(p_{0,2} - p_{0,1}\right)\right]x\right)dx = \\ &= \left(ax_{0,2} + ip_{0,2}\right)S - a\left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right)\right)\frac{b}{2a}\exp\left(\frac{b^2}{4a}\right)\left(\frac{\pi}{a}\right)^{1/2} = \\ &= \left(ax_{0,2} + ip_{0,2}\right)S - \frac{b}{2}S = \left\{\left(ax_{0,2} + ip_{0,2}\right) - \frac{\left[a\left(x_{0,1} + x_{0,2}\right) + i\left(p_{0,2} - p_{0,1}\right)\right]}{2}\right\}S = \frac{\left[a\left(x_{0,2} - x_{0,1}\right) + i\left(p_{0,2} + p_{0,1}\right)\right]}{2}S \end{aligned} \tag{4}$$

Check:

$$\begin{aligned} &D_{21} = \int\left(G_2^* \nabla G_1\right)dx = \frac{\left[a\left(x_{0,1} - x_{0,2}\right) + i\left(p_{0,1} + p_{0,2}\right)\right]}{2}S \Rightarrow \\ &\left(\int\left(G_2^* \nabla G_1\right)dx\right)^* = \frac{\left[-a\left(x_{0,2} - x_{0,1}\right) - i\left(p_{0,1} + p_{0,2}\right)\right]}{2}S = -D_{12} \end{aligned} \tag{5}$$

So:

$$D_{12}^* = -D_{21}. \tag{6}$$

5. Kinetic energy integral

$$g = \exp\left(-\frac{a}{2}\left(x - x_0\right)^2 + ip_0\left(x - x_0\right)\right) \tag{7}$$

$$g_x^{'} = \left(-a\left(x - x_0\right) + ip_0\right)G \tag{8}$$

$$\begin{aligned} g_x^{''} &= -ag + \left(-a\left(x - x_0\right) + ip_0\right)g' = -ag + \left(-a\left(x - x_0\right) + ip_0\right)^2 g = \\ &= \left(a^2\left(x - x_0\right)^2 - 2iap_0\left(x - x_0\right) - a - p_0^2\right)g \end{aligned} \tag{9}$$

$$\int G_1^* \nabla^2 G_2 dx = \left(\frac{a}{\pi}\right)^{1/2} \int \left(a^2 (x - x_{0,2})^2 - 2iap_{0,2}(x - x_{0,2}) - a - p_{0,2}^2\right) g_1^* g_2 dx = \tag{10}$$
$$= \left(-a - p_{0,2}^2\right) S_{12} + I_2 - I_1$$

$$I_2 = \left(\frac{a}{\pi}\right)^{1/2} \int a^2 (x - x_{0,2})^2 g_1^* g_2 dx =$$
$$= a^2 \left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right)\right)$$
$$\int (x - x_{0,2})^2 \exp\left(-ax^2 + \left[a(x_{0,1} + x_{0,2}) + i(p_{0,2} - p_{0,1})\right]x\right)dx =$$
$$= C\int (x - x_{0,2})^2 \exp\left(-ax^2 + bx\right)dx = C\int (x - x_{0,2})^2 \exp\left(-a\left(x - \frac{b}{2a}\right)^2 + \frac{b^2}{4a}\right)dx = \left| x' = x - \frac{b}{2a} \right| =$$
$$= C'\int \left(x' + \frac{b}{2a} - x_{0,2}\right)^2 \exp\left(-ax'^2\right)dx' = C'\left[\frac{1}{2}\left(\frac{\pi}{a^3}\right)^{1/2} + \left(\frac{b}{2a} - x_{0,2}\right)^2 \left(\frac{\pi}{a}\right)^{1/2}\right] =$$
$$= a^2 \left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right)\right) \exp\left(\frac{b^2}{4a}\right)\left[\frac{1}{2}\left(\frac{\pi}{a^3}\right)^{1/2} + \left(\frac{b}{2a} - x_{0,2}\right)^2 \left(\frac{\pi}{a}\right)^{1/2}\right] =$$
$$= a^2 \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right) + \frac{b^2}{4a}\right)\left[\frac{1}{2a} + \left(\frac{b}{2a} - x_{0,2}\right)^2\right] =$$
$$= S_{12} a^2 \left[\frac{1}{2a} + \left(\frac{b}{2a} - x_{0,2}\right)^2\right] = S_{12}\left[\frac{1a}{2} + \left(\frac{b - 2ax_{0,2}}{2}\right)^2\right] \tag{11}$$

$$C = a^2 \left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right)\right) \tag{12}$$

$$C' = C \exp\left(\frac{b^2}{4a}\right) \tag{13}$$

$$b = \left[a(x_{0,1} + x_{0,2}) + i(p_{0,2} - p_{0,1})\right] \tag{14}$$

$$I_1 = 2iap_{0,2}\left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right)\right)$$
$$\int (x - x_{0,2})\exp\left(-ax^2 + \left[a(x_{0,1} + x_{0,2}) + i(p_{0,2} - p_{0,1})\right]x\right)dx =$$
$$= C\int (x - x_{0,2})\exp\left(-ax^2 + bx\right)dx = C\int (x - x_{0,2})\exp\left(-a\left(x - \frac{b}{2a}\right)^2 + \frac{b^2}{4a}\right)dx = \tag{15}$$
$$= C'\int (x - x_{0,2})\exp\left(-a\left(x - \frac{b}{2a}\right)^2\right)dx = \left| x' = x - \frac{b}{2a} \right| = C'\int \left(x' + \frac{b}{2a} - x_{0,2}\right)\exp\left(-ax'^2\right)dx' =$$
$$= C'\left(\frac{b}{2a} - x_{0,2}\right)\left(\frac{\pi}{a}\right)^{1/2} = 2iap_{0,2}\left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right)\right)\exp\left(\frac{b^2}{4a}\right)\left(\frac{b}{2a} - x_{0,2}\right)\left(\frac{\pi}{a}\right)^{1/2} =$$
$$= 2iap_{0,2}\exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right) + \frac{b^2}{4a}\right)\left(\frac{b}{2a} - x_{0,2}\right) =$$
$$= S_{12} ip_{0,2}\left(b - 2ax_{0,2}\right)$$

$$C = 2iap_{0,2}\left(\frac{a}{\pi}\right)^{1/2} \exp\left(-\frac{a}{2}\left(x_{0,1}^2 + x_{0,2}^2\right) + i\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2}\right)\right) \tag{16}$$

$$C' = C\exp\left(\frac{b^2}{4a}\right) \tag{17}$$

$$b = \left[a\left(x_{0,1} + x_{0,2}\right) + i\left(p_{0,2} - p_{0,1}\right)\right] \tag{18}$$

So:

$$\begin{aligned}
&\int G_1^* \nabla^2 G_2 dx = \left(-a - p_{0,2}^2\right)S_{12} + I_2 - I_1 = \\
&= \left(-a - p_{0,2}^2\right)S_{12} + S_{12}\left[\frac{a}{2} + \left(\frac{b - 2ax_{0,2}}{2}\right)^2\right] - S_{12} i p_{0,2}\left(b - 2ax_{0,2}\right) = \\
&= S_{12}\left\{-a - p_{0,2}^2 + \frac{a}{2} + \frac{\left[a\left(x_{0,1} - x_{0,2}\right) + i\left(p_{0,2} - p_{0,1}\right)\right]^2}{4} - ip_{0,2}\left[a\left(x_{0,1} - x_{0,2}\right) + i\left(p_{0,2} - p_{0,1}\right)\right]\right\} = \\
&= S_{12}\left\{\begin{array}{l} -\frac{a}{2} - p_{0,2}^2 + \frac{1}{4}a^2\left(x_{0,1} - x_{0,2}\right)^2 + \frac{1}{2}ai\left(x_{0,1} - x_{0,2}\right)\left(p_{0,2} - p_{0,1}\right) - \frac{1}{4}\left(p_{0,2}^2 - 2p_{0,2}p_{0,1} + p_{0,1}^2\right) \\ -ai\left(x_{0,1} - x_{0,2}\right)p_{0,2} + p_{0,2}^2 - p_{0,2}p_{0,1} \end{array}\right\} = \\
&= S_{12}\left\{-\frac{a}{2} + a^2\left(\frac{x_{0,1} - x_{0,2}}{2}\right)^2 - \left(\frac{p_{0,2} + p_{0,1}}{2}\right)^2 - \frac{1}{2}ai\left(x_{0,1} - x_{0,2}\right)\left(p_{0,2} + p_{0,1}\right)\right\}
\end{aligned} \tag{19}$$

6. Summary

$$G = \left(\frac{a}{\pi}\right)^{1/4} \exp\left(-\frac{a}{2}\left(x - x_0\right)^2 + ip_0\left(x - x_0\right)\right), \tag{20}$$

$$S_{G,12} = \int G_1^* G_2 dx = \exp\left(-\frac{a}{4}\left(x_{0,1} - x_{0,2}\right)^2 - \frac{1}{4a}\left(p_{0,2} - p_{0,1}\right)^2\right)\exp\left(i\left(\left(x_{0,1} - x_{0,2}\right)\frac{\left(p_{0,1} + p_{0,2}\right)}{2}\right)\right) \tag{21}$$

$$\mu_{G,12} = \int G_1^* x G_2 dx = \left[\frac{\left(x_{0,1} + x_{0,2}\right)}{2} + i\frac{\left(p_{0,2} - p_{0,1}\right)}{2a}\right]S_{G,12}$$

$$D_{G,12} = \int G_1^* \nabla G_2 dx = \frac{\left[a\left(x_{0,2} - x_{0,1}\right) + i\left(p_{0,2} + p_{0,1}\right)\right]}{2}S_{G,12} \tag{22}$$

$$T_{G,12} = \int G_1^* \nabla^2 G_2 dx = S_{G,12}\left\{-\frac{a}{2} + a^2\left(\frac{x_{0,1} - x_{0,2}}{2}\right)^2 - \left(\frac{p_{0,2} + p_{0,1}}{2}\right)^2 - \frac{1}{2}ai\left(x_{0,1} - x_{0,2}\right)\left(p_{0,2} + p_{0,1}\right)\right\} \tag{23}$$

6. Generalization

The form of the Gaussian, Eq. 1, is not general – the momentum term should have the $\hbar$ denominator. In addition, the complex phase factor is often present. So the more appropriate form is

$$G = \left(\frac{a}{\pi}\right)^{1/4} \exp\left(-\frac{a}{2}\left(x - x_0\right)^2 + \frac{ip_0}{\hbar}\left(x - x_0\right) + \frac{i\gamma}{\hbar}\right) \tag{24}$$

Let also denote $\alpha = \frac{a}{2}$, so:

$$G = \left(\frac{2\alpha}{\pi}\right)^{1/4} \exp\left(-\alpha\left(x - x_0\right)^2 + \frac{ip_0}{\hbar}\left(x - x_0\right) + \frac{i\gamma}{\hbar}\right) \tag{25}$$

This form, for instance, is present in the paper of Makhov et al. [Makhov, D. V.; Glover, W. J.; Martinez, T. J.; Shalashilin, D. V. Ab Initio Multiple Cloning Algorithm for Quantum Nonadiabatic Molecular Dynamics. The Journal of Chemical Physics 2014, 141 (5), 54110.]

The results Eqs. 21-23 derived for the form Eq. 1 will transform to:

$$S_{G,12} = \int G_1^* G_2 dx = \exp\left(-\frac{\alpha}{2}\left(x_{0,1} - x_{0,2}\right)^2 - \frac{1}{8\alpha\hbar^2}\left(p_{0,2} - p_{0,1}\right)^2 + i\left(x_{0,1} - x_{0,2}\right)\frac{\left(p_{0,1} + p_{0,2}\right)}{2\hbar} + \frac{i}{\hbar}\left(\gamma_2 - \gamma_1\right) \right)$$

(26)

$$\mu_{G,12} = \int G_1^* x G_2 dx = \left[\frac{\left(x_{0,1} + x_{0,2}\right)}{2} + i\frac{\left(p_{0,2} - p_{0,1}\right)}{4\alpha\hbar} \right] S_{G,12}$$

$$D_{G,12} = \int G_1^* \nabla G_2 dx = \left[\alpha\left(x_{0,2} - x_{0,1}\right) + i\frac{\left(p_{0,2} + p_{0,1}\right)}{2\hbar} \right] S_{G,12} \quad (27)$$

$$T_{G,12} = \int G_1^* \nabla^2 G_2 dx = S_{G,12}\left\{ -\alpha + \alpha^2\left(x_{0,1} - x_{0,2}\right)^2 - \frac{1}{\hbar^2}\left(\frac{p_{0,2} + p_{0,1}}{2}\right)^2 - 2\alpha i\left(x_{0,1} - x_{0,2}\right)\frac{\left(p_{0,2} + p_{0,1}\right)}{2} \right\} \quad (28)$$

Introducing variables

$$\Delta X = x_{0,2} - x_{0,1},\ \Delta P = p_{0,2} - p_{0,1},\ \Delta\gamma = \gamma_2 - \gamma_1\ \overline{P} = \frac{p_{0,1} + p_{0,2}}{2},\ \overline{X} = \frac{x_{0,1} + x_{0,2}}{2}. \quad (29)$$

The above equations simplify to:

$$S_{G,12} = \int G_1^* G_2 dx = \exp\left(-\frac{\alpha}{2}(\Delta X)^2 - \frac{1}{8\alpha\hbar^2}(\Delta P)^2 - \frac{i\overline{P}\Delta X}{\hbar} + \frac{i\Delta\gamma}{\hbar} \right) \quad (30)$$

$$\mu_{G,12} = \int G_1^* x G_2 dx = \left[\overline{X} + \frac{\Delta P}{4\alpha\hbar} i \right] S_{G,12}$$

$$D_{G,12} = \int G_1^* \nabla G_2 dx = \left[\alpha(\Delta X) + \frac{i\overline{P}}{\hbar} \right] S_{G,12} \quad (31)$$

$$T_{G,12} = \int G_1^* \nabla^2 G_2 dx = S_{G,12}\left\{ -\alpha + \alpha^2(\Delta X)^2 - \frac{\overline{P}^2}{\hbar^2} + 2\alpha i\Delta X \cdot \overline{P} \right\} \quad (32)$$

The equations for the overlap and for the kinetic energy are consistent with those of Makhov et al. However, the equation for the derivative coupling is not – they attribute similar equation to a different type of the derivative coupling.
To show consistency of the overlap, consider

$$\frac{i}{\hbar}\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2} + \frac{x_{0,1}+x_{0,2}}{2}\left(p_{0,2} - p_{0,1}\right)\right) =$$
$$= \frac{i}{\hbar}\left(p_{0,1}x_{0,1} - p_{0,2}x_{0,2} + \frac{x_{0,1}p_{0,2}}{2} - \frac{x_{0,1}p_{0,1}}{2} + \frac{x_{0,2}p_{0,2}}{2} - \frac{x_{0,2}p_{0,1}}{2}\right) =$$
$$= \frac{i}{\hbar}\left(\frac{x_{0,1}p_{0,2}}{2} + \frac{x_{0,1}p_{0,1}}{2} - \frac{x_{0,2}p_{0,2}}{2} - \frac{x_{0,2}p_{0,1}}{2}\right) = \frac{i}{\hbar}\left(\frac{\left(x_{0,1}-x_{0,2}\right)p_{0,2}}{2} + \frac{\left(x_{0,1}-x_{0,2}\right)p_{0,1}}{2}\right) =$$
$$= -\frac{i\Delta X}{\hbar}\left(\frac{p_{0,2}+p_{0,1}}{2}\right) = -\frac{i\Delta X \cdot \overline{P}}{\hbar}$$

So, their expression coincides with our term $-\frac{i\overline{P}\Delta X}{\hbar}$