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Some integrals with Gaussian wavepackets

1. Definition

The normalized Gaussian wavepacket is defined as:

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

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

2. Overlap integral

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

Here, we have used the integral

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

3. Derivative coupling integral

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

Check:

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

So:

$$D_{12}^* = -D_{21}\,. \qquad (6)$$

4. Kinetic energy integral

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

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

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

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

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

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

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

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

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

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

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

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

So:

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

5. Summary

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

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

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

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

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

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

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

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

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:

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

(26)

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

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

Introducing variables

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

The above equations simplify to:

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

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

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

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 $-\frac{i\overline{P}\Delta X}{\hbar}$