Exact Wigner Function Evaluation for Different Basis Sets

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Abstract

In this work we present closed-form expressions for different types of Gaussian integrals that occur when evaluating the Winger function in a given basis. Wigner function represents a phase space distribution function from which positions and momentum can be, for example, sampled as initial conditions in molecular dynamics simulations. We focus on the harmonic oscillator basis and demonstrate the evaluation of the Wigner function. We also present results for the distributed Gaussian basis. Our results allows us to circumvents numerical evaluation and any imprecision associated to the procedure. Furthermore, our contribution is relevant beyond the scope of applications in quantum chemistry.

Wigner Quasiprobability Distribution – Definitions

- Definition: A function which provides a connection between the wavefunction $\Psi(\vec{x})$ (where $\vec{x} \in \mathbb{R}^3$, and is an element of the Hilbert space) defined by the stationary Schrödinger equation $\hat{H}\Psi = E\Psi$ to the probability distribution in the phase space which depends on the position $\vec{q}$ and its conjugate, the momentum $\vec{p}$. It reads

$$W(\vec{q},\vec{p}) = \frac{1}{\pi\hbar}\int_{-\infty}^{\infty} \Psi^*(\vec{q}+\vec{y})\Psi(\vec{q}-\vec{y})e^{2i\vec{p}\vec{y}/\hbar}\mathrm{d}\vec{y}. \quad (1)$$

- Lets assume that the wavefunction can be represented as a superposition of orthonormal basis states $\phi_p(\vec{x})$ as

$$\Psi(\vec{x}) = \sum_{n=0}^{Z} C_n\phi_n(\vec{x}), \quad (2)$$

where C_n are the coefficients, and Z is the number of elements.

Different Basis Sets - One-dimensional Examples

- The **quantum harmonic oscillator basis set** reads

$$\phi_n(x) = (2^n n!\sqrt{\pi})^{-1/2}\alpha^{1/2}e^{-\frac{\alpha^2x^2}{2}}H_n(\alpha x), \quad (3)$$

where we have denoted $\alpha = (\frac{m\omega}{\hbar})^{1/2}$ and H_n $(n = 0, 1, 2, \ldots, Z)$ are the Hermite polynomials defined as

$$H_n(x) = (-1)^n e^{x^2}\frac{\mathrm{d}^n}{\mathrm{d}x^n}e^{-x^2}. \quad (4)$$

Figure: First few states of the Harmonic oscillator basis when $\alpha = 1$.

- The **distributed Gaussian basis set** reads

$$\chi_\mu(x) = \sqrt[4]{\frac{2A_\mu}{\pi}}e^{-A_\mu(x-x_\mu)^2}, \quad (5)$$

where $\mu = 0, 1, 2, \ldots, Z$, $x \in \mathbb{R}$, x_μ denotes the shift in the position of the particular Gaussian and A_μ is a normalizing constant.

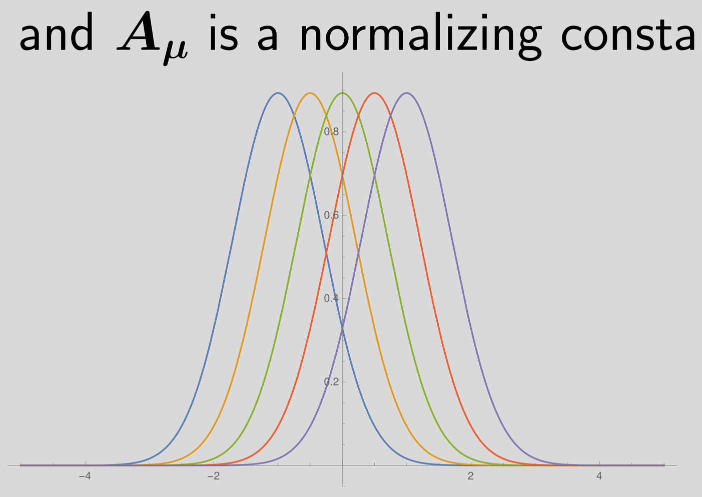

Figure: Examples of distributed (shifted) Gaussians of equal amplitude and width.

- Both basis set examples feature a Gaussian and in order to evaluate the Wigner function in Eq. (1) we resort to multiple and different variable transformations, completing the square and the binomial expansion

$$(x+y)^n = \sum_{k=0}^{n}\binom{n}{k}x^{n-k}y^k. \quad (6)$$

Results – Quantum Harmonic Oscillator Basis Set

$$W(q,p) = \frac{\alpha e^{-\alpha^2q^2+\frac{\beta^2}{4\alpha^2}}}{2\pi^{3/2}\hbar}\sum_{p=0}^{Z}\sum_{k=0}^{Z}C_pC_k(2^{p+k})^{-1/2}(p!k!)^{1/2}$$
$$\times\sum_{m=0}^{\lfloor p/2\rfloor}\sum_{m'=0}^{\lfloor k/2\rfloor}\frac{(-1)^{m+m'}(2\alpha)^{p+k-2(m+m')}}{m!m'!(p-2m)!(k-2m')!}\sum_{s=0}^{p-2m}\sum_{s'=0}^{k-2m'}\binom{p-2m}{s}\binom{k-2m'}{s'}$$
$$\times q^{p+k-2(m+m')-(s+s')}\frac{(-1)^{s'}}{\alpha^{1+s+s'}}\sum_{s''=0}^{s+s'}\binom{s+s'}{s''}\Big(\frac{\beta}{2\alpha}\Big)^{s''}\times$$
$$\Big(1+(-1)^{s+s'-s''}\Big)\Gamma\Big(\frac{1+s+s'-s''}{2}\Big), \quad \text{while} \quad s+s'-s'' > -1 \quad (7)$$

- Wigner function is evaluated exactly below for different basis coefficients C_n where $n = 0, 1, \ldots Z$ and $Z = 10$
  - $C_0 = 1$, while $C_{n\neq 0} = 0$ (upper left),
  - $C_1 = 1$, while $C_{n\neq 0} = 0$ (upper right),
  - $C_2 = 1$, while $C_{n\neq 0} = 0$ (lower left),
  - $\{C_0, \ldots, C_{10}\} = \{1, 6, 1, 8, 0, 3, 3, 9, 8, 8\}$ golden mean (lower right)

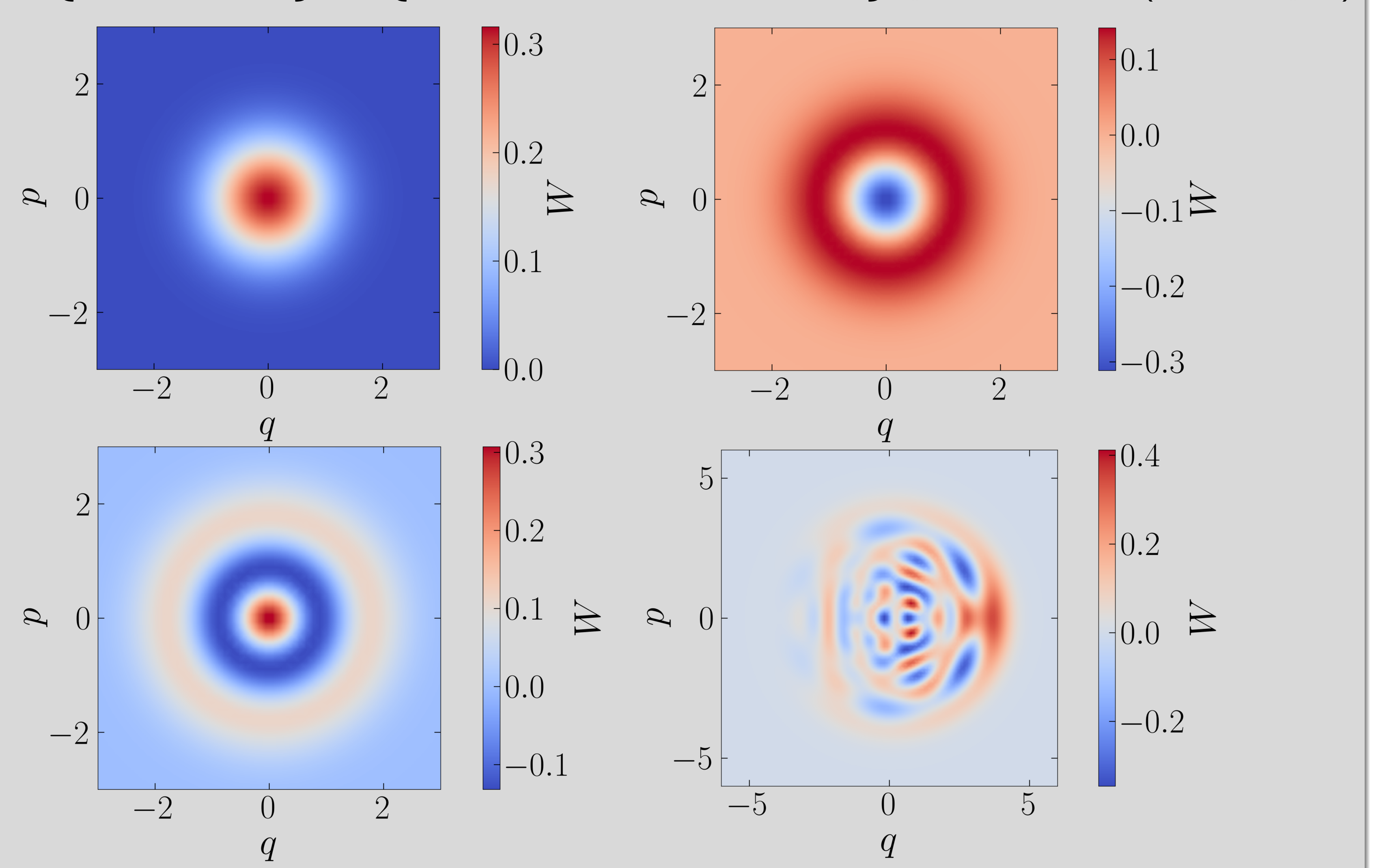

Figure: Heatmap of $W(q,p)$ for different cases. We fix $\alpha = 1.0$ and $\hbar = 1.0$. Purely analytical evaluation, no numerical evaluation of integrals required.

- Wigner function integration over momentum and position

$$W(p) = \int_{\mathbb{R}^2} W(q,p)\mathrm{d}q, \quad \text{and} \quad W(q) = \int_{\mathbb{R}^2} W(q,p)\mathrm{d}p. \quad (8)$$

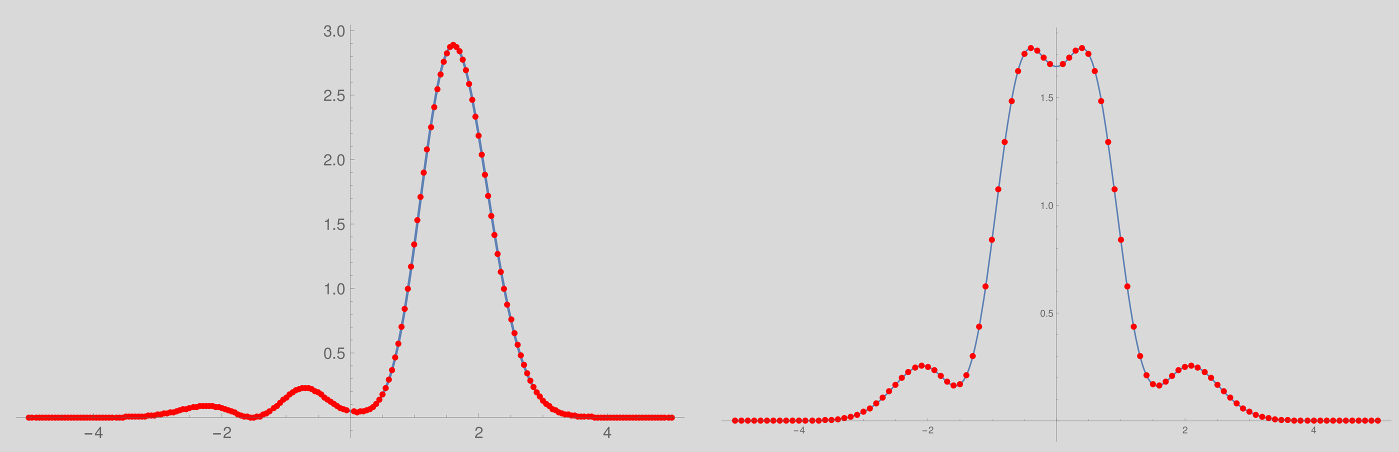

Figure: We fix $\alpha = 1.0$, $\hbar = 1.0$ and $Z = 3$ where we set all C_k and C_p to 1. Numerical (red dots) vs analytical (blue line) evaluation of $W(p)$ (left) and $W(q)$ (right).

Results – Distributed Gaussian Basis Set

$$W(q,p) = \frac{4^{1/4}}{\pi\hbar}\sum_{p=0}^{Z}\sum_{k=0}^{Z}C_pC_k\Big(A_kA_p\Big)^{1/4}(A_p+A_k)^{-1/2}e^{\frac{(2q(A_k-A_p)+2(x_p-x_k)+\beta)^2}{4(A_p+A_k)}}$$
$$\times\, e^{-q^2(A_p+A_k)+2q(A_px_p+A_kx_k)-(A_px_p^2+A_kx_k^2)} \quad (9)$$

Conclusion

- We obtained closed-form expressions for the Wigner function for two different and commonly used orthonormal basis sets. Exact expressions have a wide scope of applications in physics and chemistry.
- These results open the door to treating anharmonicities using methods such Vibrational Self-Consistent Field (VSCF) approximation of increasing dimensionality.

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Hybrid Scale

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