Comparison with exact overlap integrals

Here, we calculate overlap integrals between two harmonic-oscillator eigenfunctions and compare results with above estimations found by projecting Wigner transform onto the energy surface.

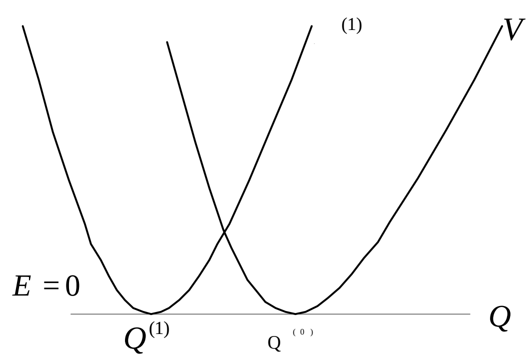
Propensity rules are not of our concern here because the initial and final states are defined in advance. Without loss of generality one can consider one-dimensional oscillator. For many-dimensional harmonic oscillator, matrix elements can be found as a product of one-dimensional integrals.

Overlap integral at *E* = 0

A donor and an acceptor Hamiltonians are

$$H = \frac{1}{2}\left[P^2 + \omega^{(0)2}\left(Q - Q^{(0)}\right)^2\right]$$
$$H^{(1)} = \frac{1}{2}\left[P^2 + \omega^{(1)2}\left(Q - Q^{(1)}\right)^2\right] \qquad (30)$$

(we set $m = 1$). Schematically, the potentials are shown below



.

Since acceptor energy surface shrinks to one point at the potential bottom, both acceptor and donor are in a ground state,

$$\begin{aligned}\psi &= \left(\frac{\omega^{(0)}}{\pi}\right)^{1/4} \exp\left(-\frac{\omega^{(0)}}{2}\left(Q-Q^{(0)}\right)^2\right) \\ \psi^{(1)} &= \left(\frac{\omega^{(1)}}{\pi}\right)^{1/4} \exp\left(-\frac{\omega^{(1)}}{2}\left(Q-Q^{(1)}\right)^2\right)\end{aligned}, \tag{31}$$

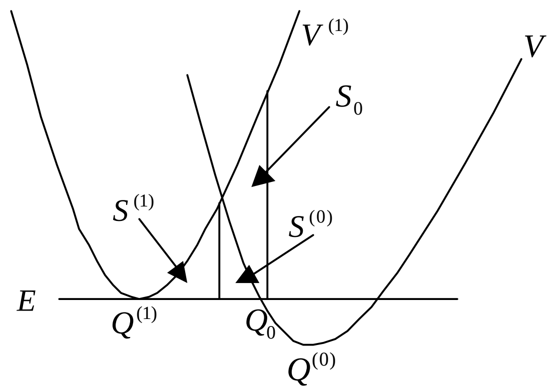
and the overlap integral is

$$A = \int_{-\infty}^{\infty} \psi(Q)\psi^{(1)}(Q)dq = \sqrt{2}\,\frac{\left(\omega^{(0)}\omega^{(1)}\right)^{1/4}}{\left(\omega^{(0)}+\omega^{(1)}\right)^{1/2}} \exp\left(-\tfrac{1}{2}\frac{\omega^{(0)}\omega^{(1)}}{\omega^{(0)}+\omega^{(1)}}\left(Q^{(0)}-Q^{(1)}\right)^2\right). \tag{32}$$

According to the method of Wigner transform, A^2 is approximated by the function $\rho(P,Q)$ at accepting point $(P,Q)=(0,Q^{(1)})$. There, $W=-\tfrac{1}{2}\ln\rho=\tfrac{1}{2}\omega^{(1)}\left(Q^{(0)}-Q^{(1)}\right)^2$. However according to exact calculations, the exponential factor $-\tfrac{1}{2}\ln A^2$ is different, $\tfrac{1}{2}\frac{\omega^{(0)}\omega^{(1)}}{\omega^{(0)}+\omega^{(1)}}\left(Q^{(0)}-Q^{(1)}\right)^2$, see Eq. (32). For example, if frequencies are equal, the former exponential factor is two times larger than the latter one. If the frequency $\omega^{(0)}$ is large, then the factors are almost the same. By doing projection of the Wigner-function on the accepting point we are approximating in effect the acceptor wavefunction by δ -function, $\psi^{(1)}(Q)=\delta(Q-Q^{(1)})$.

Quasiclassical overlap integral

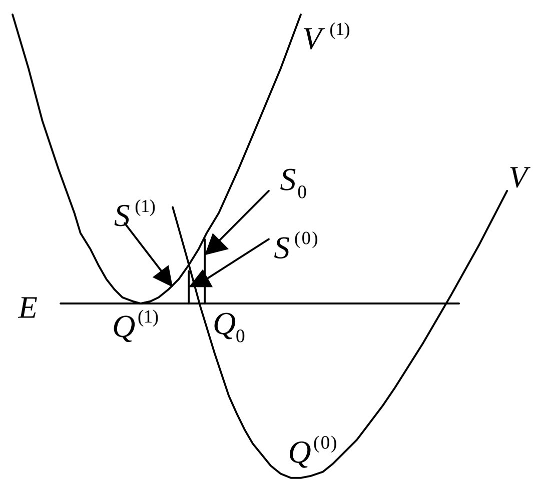
Generally, an overlap integral can be estimated quasiclassically, without a pre-factor, as an exponent of integral of action over forbidden region which is a sum of $S^{(0)}$ and $S^{(1)}$, see a figure below.



.

It is easy to see that S_0 is always larger that the sum of $S^{(0)}$ and $S^{(1)}$. So, the logarithm of Wigner-function is always larger than the quasiclassical exponential factor (as long as momentum of the accepting point is zero).

When the transition is almost allowed classically (so called reflection approximation), then $S^{(1)} >> S^{(2)}$, see a figure below,



and there is good agreement with quasiclassical approximation. This inequality generally holds when derivative of V is much larger than derivative of $V^{(1)}$ at the point of crossing of potentials.

Direct calculation of an overlap integral between two harmonic-oscillator wave functions

Since the harmonic oscillator is an exactly solvable problem, we can estimate explicitly an overlap integral between two wavefunctions $\psi_0(x) = \varphi_0(\omega_0, x)$ and $\psi_1(x) = \varphi_{n_1}(\omega_1, x-a)$ where

$$\varphi_n(\omega, x) = \left(\frac{\omega}{\pi\hbar}\right)^{1/4} \frac{1}{2^{n/2}\sqrt{n!}} \exp\left(-\tfrac{1}{2}\omega x^2/\hbar\right) H_n\left(x\sqrt{\omega/\hbar}\right) \tag{1}$$

is an eigenfunction of a harmonic oscillator. Here, $\psi_0(x)$ is a ground-state wavefunction of the donor state, $\psi_{n_1}(x)$ is an excited-state wavefunction of the acceptor state, and a is a shift along x-axis between bottoms of harmonic potentials. one in order to consider later a quasiclassical limit $\hbar \to 0$. We calculated the overlap integral

$$I_{n_1}(\omega_0, \omega_1, a) = \int_{-\infty}^{\infty} \psi_0(x)\psi_1(x)dx \tag{2}$$

for successively increasing n_1 by *Mathematica* software and finally we guess a general formula (valid for any n_1):

$$I_{n_1}(\omega_0, \omega_1, a) = (n_1!)^{1/2} \frac{\omega_0^{1/4}\omega_1^{1/4}}{(\omega_0+\omega_1)^{n_1+1/2}} \exp\left(-\frac{1}{2}\frac{a^2}{\hbar}\frac{\omega_0\omega_1}{\omega_0+\omega_1}\right) \sum_{i=0}^{[n_1/2]} \frac{2^{n_1/2+1/2-2i}}{i!(n_1-2i)!} \left(\omega_1^2-\omega_0^2\right)^i \left(\frac{\hbar}{a^2\omega_0^2\omega_1}\right)^{i-n_1/2}, \tag{3}$$

where $[n_1/2]$ is the largest integer smaller or equal to $n_1/2$. We tested that the formula (3) for all $n_1 \le 20$, and we expect that it is valid for arbitrary n_1.

$\hbar \to 0$ **limit**

Let us estimate the quasiclassical limit of the overlap integral by substituting $n_1 = E/(\hbar\omega_1)$ into the expression (3) and setting $\hbar \to 0$.

Equal frequencies

Consider firstly the case $\omega_0 = \omega_1 = \omega$. Because of presence of successive powers of $\left(\omega_1^2 - \omega_0^2\right)$ in (3), there is only one nonzero term in the sum, and

$$I_{n_1}(\omega,\omega,a) = \left(n!\right)^{-1/2}\left(\frac{a^2\omega}{2\hbar}\right)^{n_1/2}\exp\left(-\frac{a^2\omega}{4\hbar}\right), \tag{4}$$

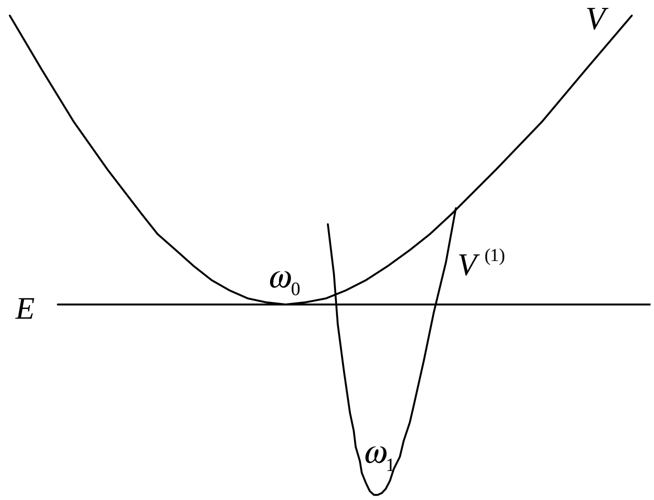
Using Stirling formula for the factorial in (4), we find

$$I_{n_1}(\omega,\omega,a)\xrightarrow[\hbar\to 0]{}\left(\frac{\hbar\omega}{2\pi E}\right)^{1/4}\exp\left(-\frac{E}{2\omega\hbar}\left[1-\frac{a^2\omega^2}{2E}+\ln\left(\frac{a^2\omega^2}{2E}\right)\right]\right), \tag{5}$$

The exponential factor $\frac{E}{2\omega}\left[1-\frac{a^2\omega^2}{2E}+\ln\left(\frac{a^2\omega^2}{2E}\right)\right]$ is the same as the integral of action that was mentioned in a previous section.

Unequal frequencies

Now, let us consider much more complicated case $\omega_0 < \omega_1$. In this case, there are two intersections of the potential curves, see a figure below.



Let us define a function

$$f(c,n)=\sum_{i=0}^{[n/2]}\left(\frac{c}{8n}\right)^i\frac{1}{i!(n-2i)!} \qquad (6)$$

(the sum (6) can be expressed through confluent hypergeometric function $U(a,b,z)$ as $(-2n/c)^{n/2}n!U(-n/2,1/2,-2n/c)$, but this expression is not used here). We estimate the function (6) for large n by replacing the sum by an integral $\int_0^{[n/2]}\exp(-g(x))dx$ where

$$g(x)=-\ln(2\pi)+x[\ln n-\ln(c/8)+\ln x]+x-n+\tfrac{1}{2}\ln x+\tfrac{1}{2}\ln(n-2x)+(n-2x)\ln(n-2x).. \qquad (7)$$

After expanding the exponent around the point $x_0=\tfrac{1}{2}\left(\sqrt{1+c}-1\right)^2 n/c$, which is close to its minimum, we estimate the integral as

$$\int_{-\infty}^{\infty}\exp\left(-(g_0+g_1(x-x_0)+g_2(x-x_0)^2\right)dx=\frac{\sqrt{\pi}}{\sqrt{g_2}}\exp\left(-g_0+\frac{g_1^2}{4g_2}\right). \qquad (8)$$

We expand coefficients: $g_0=(n-1)\ln n+ng_0^{(0)}+g_0^{(1)}+O\left(\tfrac{1}{n}\right)$, $g_1=O\left(\tfrac{1}{n}\right)$, $g_2=g_2^{(0)}\left(\tfrac{1}{n}\right)+O\left(\tfrac{1}{n^2}\right)$ and after inserting them into (8) we estimate it as

$$f(c,n) \sim \frac{n^{-n-1/2}}{\sqrt{\pi}} C_0 \exp(An), \tag{9}$$

where $C_0 = \frac{\pi}{\sqrt{g_2^{(0)}}} \exp\left(g_0^{(1)}\right)$ and $A = g_0^{(0)}$. Inserting there expressions for expansion coefficients (which are omitted here), we find:

$$\begin{aligned} C_0 &= \tfrac{1}{2}\left[\frac{c}{c_1(c_1-1)}\right]^{1/2} \\ A &= \tfrac{1}{2} + \frac{c_1-1}{c} + \ln\left(\frac{c}{2(c_1-1)}\right) \end{aligned}, \tag{10}$$

where $c_1 = (1+c)^{1/2}$. Eq. (9) was proven for positive c, but numerical tests show that it is correct for a wider range $c > -1$, although a proof for the range $-1 < c < 0$ is unknown. Numerical tests show that for $c < -1$, a modified Eq. (9) holds,

$$f(c,n) \sim \frac{n^{-n-1/2}}{\sqrt{\pi}} 2\,\mathrm{Re}\left(C_0 \exp(An)\right), \tag{9a}$$

where C_0, A, and c_1 are defined by the same formulas (10). In these formulas, one should choose any branch of $(1+c)^{1/2}$, any branch of $\ln\left(\frac{c}{2(c_1-1)}\right)$, and a branch with a positive real part of $\left[\frac{c}{c_1(c_1-1)}\right]^{1/2}$. Approximations (9) and (9a) became poorer as $c \to -1$. A special case of $c = -1$ remains to be studied.

Now, let us use Eq. (9) to estimate the overlap integral. Using (3) and Stiltjes formula for $n!$, it can be expressed through the function (6) as

$$I_n(\omega_0,\omega_1,a) = \left(2\sqrt{2\pi n}(n/e)^n\right)^{1/2} \frac{\omega_0^{1/4}\omega_1^{1/4}}{(\omega_0+\omega_1)^{n+1/2}} \exp\left(-\tfrac{1}{2}\frac{a^2}{\hbar}\frac{\omega_0\omega_1}{\omega_0+\omega_1}\right)\left(2a^2\omega_0^2\omega_1/\hbar\right)^{n/2} f(c,n). \tag{11}$$

with

$$c = \frac{2n\hbar(\omega_1^2 - \omega_0^2)}{a^2\omega_0^2\omega_1}\,. \tag{12}$$

Using (9), we find

$$\begin{aligned} &I_n(\omega_0,\omega_1,a) = (2\pi n)^{-1/4} k^{1/4} (1+k)^{-1/2} \left[\frac{c}{c_1(c_1-1)}\right]^{1/2} \exp(-Sn), \\ &S = k/c - c_1/c + \ln(c_1-1) - \tfrac{1}{2}\ln\left(c\,\frac{k-1}{k+1}\right) \end{aligned}\,. \tag{13}$$

where c given by (12), $c_1 = (1+c)^{1/2}$, and $k = \omega_1/\omega_0$. Note that in a quasiclassical limit $c = \dfrac{2E(\omega_1^2 - \omega_0^2)}{a^2\omega_0^2\omega_1^2}$. The factor S should be the same as the total quasiclassical action $S^{(0)} + S^{(1)}$.

Results of calculations by the quasiclassical formula are shown in the following table. There, we put $n = 100$, $\hbar = 0.01$, and ω_0, ω_1, a to random numbers in [0,1] interval.

ω_0	ω_1	a	$I_n(\omega_0,\omega_1,a)$	$I_n(\omega_0,\omega_1,a)$ -quasicl.
0.57457	0.76515	0.89235	1.04325×10^{-8}	1.04400×10^{-8}
0.07629	0.65783	0.39817	0.000109219	0.000109351
0.17852	0.08602	0.61838	-6.6607×10^{-24}	-6.6701×10^{-24}
0.81800	0.93198	0.25614	1.27715×10^{-37}	1.27840×10^{-37}
0.63402	0.23278	0.60826	2.92796×10^{-17}	2.93199×10^{-17}
0.03405	0.05934	0.89911	2.24516×10^{-21}	2.24779×10^{-21}
0.98540	0.16032	0.93228	-5.2161×10^{-8}	-5.2227×10^{-8}
0.64887	0.93633	0.36573	3.8282×10^{-21}	3.8322×10^{-21}
0.35771	0.88372	0.04398	3.9163×10^{-19}	3.8994×10^{-19}
0.28944	0.69988	0.48555	4.2442×10^{-11}	4.2491×10^{-11}
0.86545	0.20341	0.08150	6.0847×10^{-12}	6.0922×10^{-12}
0.66755	0.93347	0.94728	0.0000128217	0.0000128307
0.44748	0.43477	0.32522	5.5197×10^{-76}	5.5299×10^{-76}
0.91323	0.38814	0.53566	1.56263×10^{-20}	1.56651×10^{-20}
0.33982	0.75291	0.45586	2.75723×10^{-12}	2.76038×10^{-12}
0.88679	0.40349	0.38718	2.62264×10^{-22}	2.62695×10^{-22}
0.09815	0.00307	0.35952	-0.0068781	-0.0068867
0.09774	0.39827	0.51752	5.1047×10^{-8}	5.1109×10^{-8}
0.49406	0.89433	0.31677	6.9944×10^{-18}	7.0024×10^{-18}
0.84997	0.56059	0.94705	-6.0991×10^{-23}	-6.1179×10^{-23}
0.86930	0.41520	0.23537	1.10585×10^{-23}	1.10718×10^{-23}
0.03382	0.48116	0.87954	0.0103642	0.0103769
0.89555	0.28091	0.02531	-8.7258×10^{-16}	-8.7366×10^{-16}
0.99275	0.49205	0.89374	-2.80426×10^{-19}	-2.80959×10^{-19}
0.92716	0.98968	0.13254	7.7752×10^{-57}	7.7833×10^{-57}
0.79600	0.52889	0.47216	2.19444×10^{-33}	2.19875×10^{-33}
0.63848	0.90167	0.21211	1.01601×10^{-28}	1.01717×10^{-28}
0.62219	0.07789	0.95462	1.20166×10^{-6}	1.20324×10^{-6}
0.34281	0.20699	0.84252	-8.6559×10^{-29}	-8.6709×10^{-29}
0.92079	0.86165	0.32744	2.00982×10^{-60}	2.01753×10^{-60}
0.94697	0.63988	0.83634	8.3385×10^{-25}	8.3550×10^{-25}
0.33469	0.45492	0.74614	8.2569×10^{-17}	8.2644×10^{-17}
0.90919	0.34501	0.32238	-2.13439×10^{-18}	-2.13726×10^{-18}
0.95015	0.38030	0.87285	7.1358×10^{-17}	7.1435×10^{-17}
0.68391	0.04848	0.16819	0.000086255	0.000086360
0.25067	0.60602	0.09386	1.01636×10^{-18}	1.01753×10^{-18}
0.82538	0.04368	0.76349	-0.00081810	-0.00081918
0.17307	0.96373	0.71624	0.00129971	0.00130125
0.81652	0.53319	0.12739	6.4837×10^{-36}	6.4887×10^{-36}
0.38154	0.36160	0.78705	1.91938×10^{-35}	1.95664×10^{-35}

For $c < -1$, we take real part and double the result of (13), according to Eq. (9a).

Conclusions

There exist several basic differences between phase space distribution approach and quasiclassical approach. The former approach approximates a positive quantity of square of an overlap integral, while the latter approach approximates an integral itself. If there are no potential curve crossings (when $c = \frac{2n\hbar(\omega_1^2 - \omega_0^2)}{a^2\omega_0^2\omega_1} < -1$), then an overlap integral is a rapidly oscillating function of $1/\hbar$ due to presence of an imaginary part in S, but the phase-space approximation gives a smooth function. Finally, the phase-space approximation is always smaller (at least for cases depicted on above figures) because the exponent is larger, but this error can be corrected in principle by taking into account the derivative of the potential of an acceptor surface which is equivalent to approximating of the Wigner density by Airy function instead of δ -function.