Reconsidering the model of two coupled harmonic oscillators

Hamiltonian of the model

This model Hamiltonian is from the paper of B. S. and E. J. H., J. Chem. Phys. **112**, 4004. The acceptor Hamiltonian is

$$H_{\mathrm{f}} = \tfrac{1}{2}\left(p_x^2 + p_y^2 + x^2 + y^2\right),$$

and the donor Hamiltonian is

$$H_{\mathrm{i}} = \tfrac{1}{2}\left[p_x^2 + p_y^2 + \omega_x^2 (x - x_0)^2 + \omega_y^2 (y - y_0)^2\right].$$

The final-state wave function is defined according to the formula

$$\Psi_{\mathrm{f}}(x, y) = \sum_{j=0}^{n} C_j \psi_j(x) \psi_{n-j}(y),$$

where

$$\psi_i(q) == \pi^{-1/4} \frac{1}{2^{i/2}\sqrt{i!}} \exp\left(-\tfrac{1}{2} q^2\right) H_n(q),$$

$$C_j = I_j(\omega_x, 1, x_0) I_{n-j}(\omega_y, 1, y_0),$$

and

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

Revising examples from the paper

There are 6 examples considered in the paper, but no comparison with phase-space results. Now for those examples, we calculate partial energies

$$E_x = \left(\sum_{j=0}^{n} C_j^2\right)^{-1} \sum_{j=0}^{n} C_j^2 \left(j+\tfrac{1}{2}\right),\ E_y = \left(\sum_{j=0}^{n} C_j^2\right)^{-1} \sum_{j=0}^{n} C_j^2 \left(n-j+\tfrac{1}{2}\right),$$

and their classical counterparts

$$E_x^* = \tfrac{1}{2}\left(p_x^{*2} + x^{*2}\right),\ E_y^* = \tfrac{1}{2}\left(p_y^{*2} + y^{*2}\right),$$

where p_x^*, x^*, p_y^*, y^* are phase space coordinates of minimum of Wigner function.

Figure	Parameters	R_x (%) $n=2$	R_x (%) $n=6$	R_x (%) $n=12$	R_x (%) $n=20$	R_x (%) $n=30$
1	$\omega_x = 0.02$, $\omega_y = 0.18$, $x_0 = y_0 = 0$	60.4 100.0^*	74.0 100.0^*	82.5 100.0^*	91.6 100.0^*	94.5 100.0^*
2	$\omega_x = 10$, $\omega_y = 2.2$, $x_0 = y_0 = 0$	71.8 100.0^*	87.8 100.0^*	93.8 100.0^*	96.3 100.0^*	97.5 100.0^*
3	$\omega_x = 0.45$, $\omega_y = 0.01$, $x_0 = y_0 = 0$	25.3 0.0^*	10.4 0.0^*	5.4 0.0^*	3.3 0.0^*	2.2 0.0^*
4	$\omega_x = 2$, $\omega_y = 18$, $x_0 = y_0 = 0$	24.8 0.0^*	10.1 0.0^*	5.2 0.0^*	3.2 0.0^*	2.2 0.0^*
5	$\omega_x = 2$, $\omega_y = 0.1$, $x_0 = 3, y_0 = 0$	82.6 100.0^*	82.0 71.2^*	44.9 38.4^*	27.2 23.7^*	18.3 16.1^*
6	$\omega_x = 2$, $\omega_y = 10$, $x_0 = 3, y_0 = 0$	82.6 100.0^*	82.0 71.2^*	44.9 38.4^*	27.2 23.7^*	18.3 16.1^*

Quantities that are compared are percentage of energy going to x -mode, exact versus quantum,

$$R_x = E_x / E\ ,\ R_x^* = E_x^* / E\ ,$$

where $E = n+1$. It was found (see a table above) that R_x and R_x^* agree within 10% for all examples for $n \geq 20$. Note that examples 5 and 6 are equivalent in respect to interchange of y and p_y .

New examples

Several new examples with randomly chosen parameters of potentials were considered. Generally, there is some correlation between quantum and phase-space partitions of the energy. For some examples, agreement appears very good or very bad, see the table below.

Agreement	Parameters	R_x (%) $n=2$	R_x (%) $n=6$	R_x (%) $n=12$	R_x (%) $n=20$	R_x (%) $n=30$	R_x (%) $n=31$
Worst	$\omega_x = 0.04689$, $\omega_y = 0.05555$, $x_0 = 0.1519$, $y_0 = 0.2649$	50.6 75.0*	51.5 86.5*	52.7 91.9*	54.4 94.6*	56.5 96.2*	40.4 96.3*
Best	$\omega_x = 0.5707$, $\omega_y = 0.5647$, $x_0 = 0.9740$, $y_0 = 0.9398$	50.82 51.36*	50.76 50.85*	50.36 50.32*	49.84 49.78*	49.27 49.24*	

The first line in the table is a counterexample for the phase-space method. When n changes between 0 and 40, the percentage of energy going to x -mode changes between 50% and 59% for even n and between 35% and 42% for even n while phase space prediction changes between 55% and 97%. There is only 5% agreement for $n=0$. For larger n results disagree by more than 30% (except by 25% for $n = 2$). It is interesting, that for this example the final wave function for large n collapses to a point close to the origin.