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Dept. of Chemistry

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Alexey V. Sergeev a

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and Bilha Segev

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34105, Israel

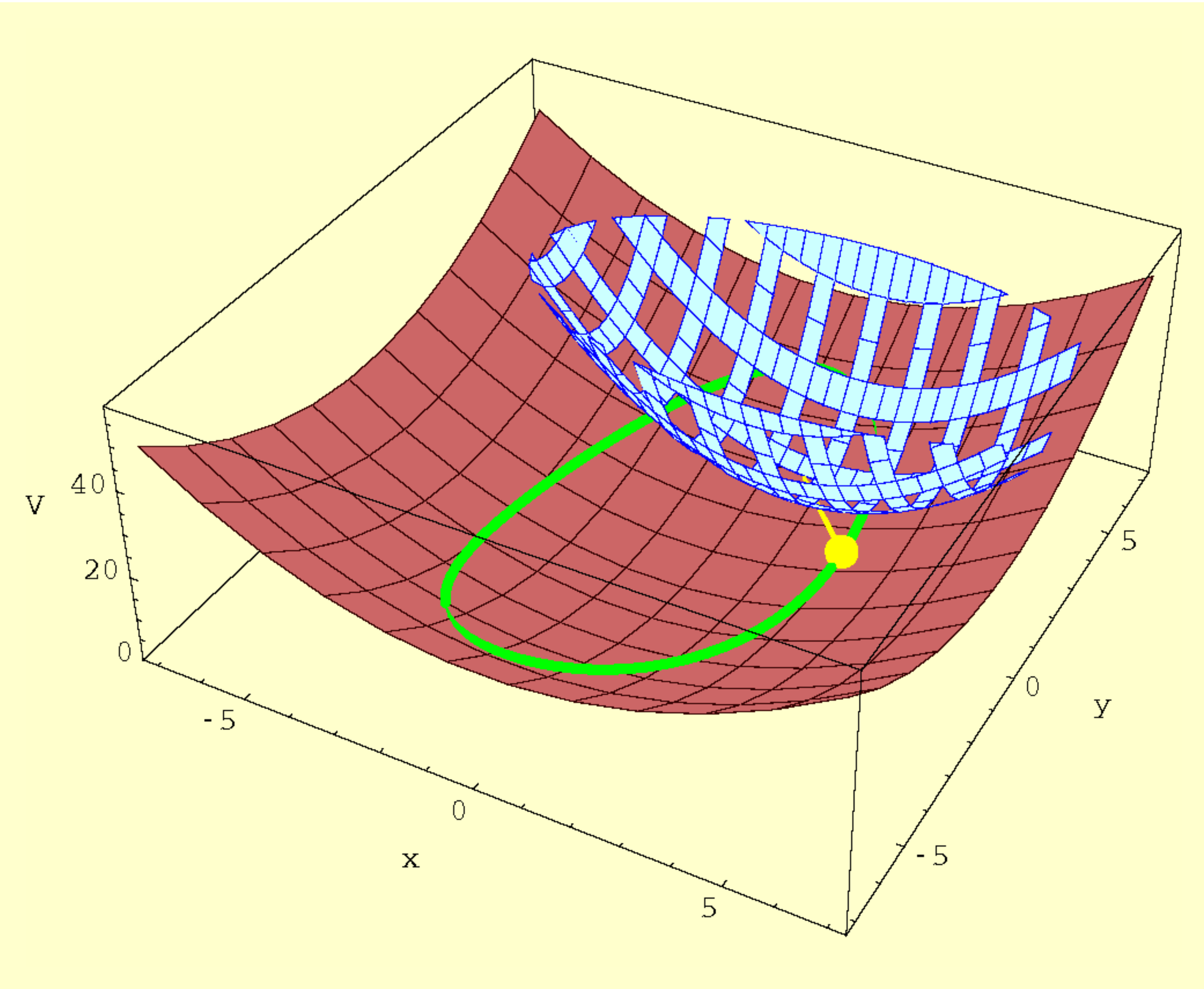
Introduction

We study a radiationless transition in a polyatomic molecule. The molecule originally vibrates around the minimum of Born – Oppenheimer surface corresponding to some excited electronic state. During the transition the electronic energy transfers to vibrational degrees of freedom of nuclei moving on the lower surface corresponding to the ground electronic state.

The subject of this study is the Franck – Condon integral, or an overlap integral between nuclear components of the molecular wavevefunctions in the initial (I) and final (F) states. It is the most important factor entering the expression for the transition rate, and it could vary by many orders of magnitude because of the tunneling nature of the transition.

In the quasiclassical approximation (the limit of small $\hbar$), the classically forbidden transition occurs at the complex-valued point in the phase space $(\vec{q}_0, \vec{p}_0)$ that is the stationary point of the classical action. Within recently developed phase-space approach based on Wigner transformation, the transition occurs at the real point in the phase space $(\vec{q}_*, \vec{p}_*)$ on the surface of constant energy where the Wigner function is maximal. Results are illustrated on two one-dimensional examples, when the donor is a harmonic oscillator and when the acceptor is (1) Morse and (2) Poeschl – Teller oscillators.

For multidimensional problems the quasiclassical (Landau) approach is difficult to apply while the phase-space method easily generalizes. Examples for two-dimensional harmonic and anharmonic oscillators are given.



Plots of the donor potential (blue porous surface) and the acceptor potential (brown solid surface) as functions of two coordinates, *x* and *y*. Yellow line (sometimes short or hidden) marks the jumping path. Green line on the acceptor surface is the classical trajectory starting from the leakage point.

http://www.bgu.ac.il/~sergeev/files/bgu/seghell/harmcalc.htm

Franck – Condon factor

$$\left| \int d\vec{q}\, \psi_{\mathrm{I}}^{*}(\vec{q}) \psi_{F}(\vec{q}) \right|^{2} = (2\pi)^{N} \int d\vec{q} \int d\vec{p}\, \rho_{\mathrm{I}}(\vec{q},\vec{p})\, \rho_{F}(\vec{q},\vec{p})$$

N-dimensional

Wigner function

$$\rho(\vec{q},\vec{p}) = \left(\frac{1}{2\pi} \right)^{N} \int d\vec{\eta}\, e^{-i\vec{p}\cdot\vec{\eta}} \psi^{*}\left(\vec{q} + \frac{\vec{\eta}}{2} \right) \psi\left(\vec{q} - \frac{\vec{\eta}}{2} \right)$$

Initial distribution

$$\rho_{\mathrm{I}}(\vec{q},\vec{p}) = \frac{1}{\pi\hbar} C(\vec{q},\vec{p}) e^{-\frac{2}{\hbar}W(\vec{q},\vec{p})}$$

Harmonic approximation:

$$V_{\mathrm{I}}(\vec{q}) = \frac{1}{2}\sum_{i=1}^{N} \omega_i^2 q_i^2$$

$$W_0(\vec{q},\vec{p}) = \frac{1}{2}\sum_{i=1}^{N}\left(\frac{1}{\omega_i} p_i^2 + \omega_i q_i^2\right)$$

$$C(\vec{q},\vec{p}) = 1$$

Anharmonic corrections (perturbative treatment):

$$V_{\mathrm{I}}(\vec{q}) = \frac{1}{2}\sum_{i=1}^{N} \omega_i^2 q_i^2 + \frac{1}{6}\sum_{i,j,k=1}^{N} v_{ijk} q_i q_j q_k$$

$$W = W_0 + W_1$$

Final distribution

Leading order:

$$\rho_F(\vec{q},\vec{p}) = \delta\left(H_{\mathrm{F}}(\vec{q},\vec{p}) - E\right)$$

Leading + first order:

$$\rho_F(\vec{q},\vec{p}) = \exp\left(-(H-E)f_2/3f_3 - 2\hbar^2 f_2^3/27f_3^2\right)\mathrm{Ai}\left(\alpha(H-E+\hbar^2 f_2^2/f_3)\right)$$

$$\alpha = \left(3\hbar^2 f_3\right)^{-1/3}$$

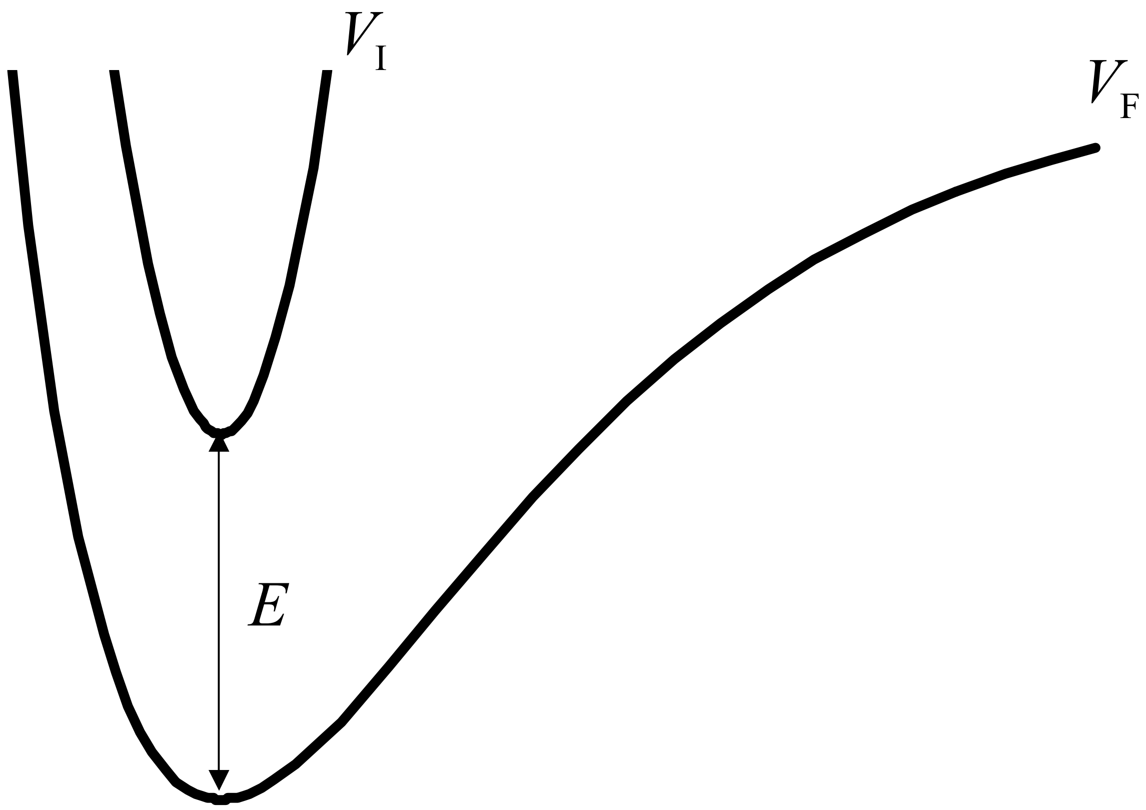
$$f_2 = \frac{1}{8}\sum_{i=1}^{N} V_{ii}''/m_i$$

$$f_3 = \frac{1}{24}\sum_{i=1}^{N}(V_i')^2/m_i + \frac{1}{24}\sum_{i,k=1}^{N} V_{ik}''\,p_i p_k/(m_i m_k)$$

Harmonic → Morse

$$H_{\mathrm{I}}(q,p) = \tfrac{1}{2}p^2 + \tfrac{1}{2}\omega^2 q^2$$

$$H_{\mathrm{F}}(q,p) = \tfrac{1}{2}p^2 + \tfrac{1}{2}\left(J+\tfrac{1}{2}\right)\left(1-e^{-\beta q}\right)^2, \quad \beta = \left(J+\tfrac{1}{2}\right)^{-1/2}$$



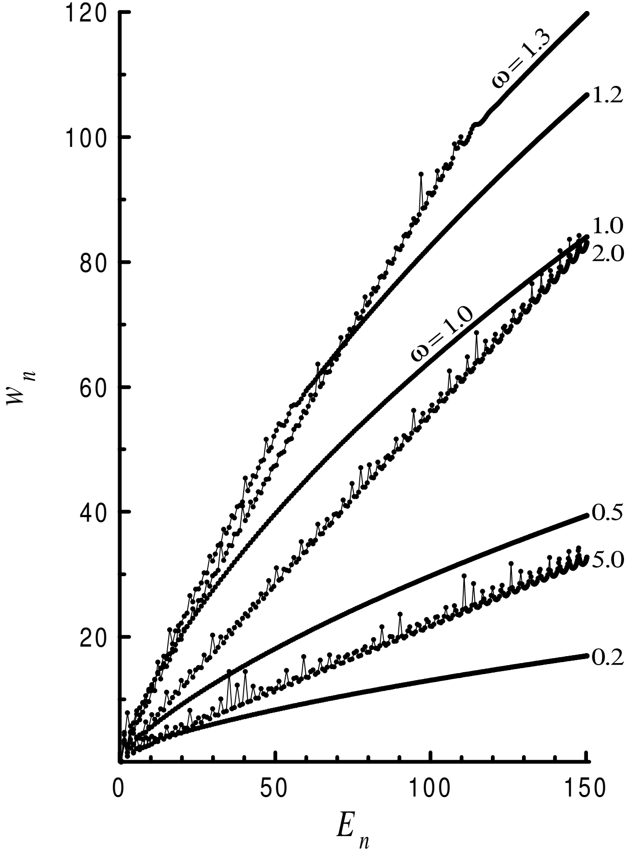


FIG. 1: Logarithm of Franck - Condon factor found by numerical integration with exact wavefunctions at the points of discrete spectrum, $E = E_n$, $n = 0, 1, \ldots, J-1$. The number of bound states is $J = 300$. Curves are labelled by values of the oscillator frequency ω. We use dimensionless units where $\hbar = 1$.

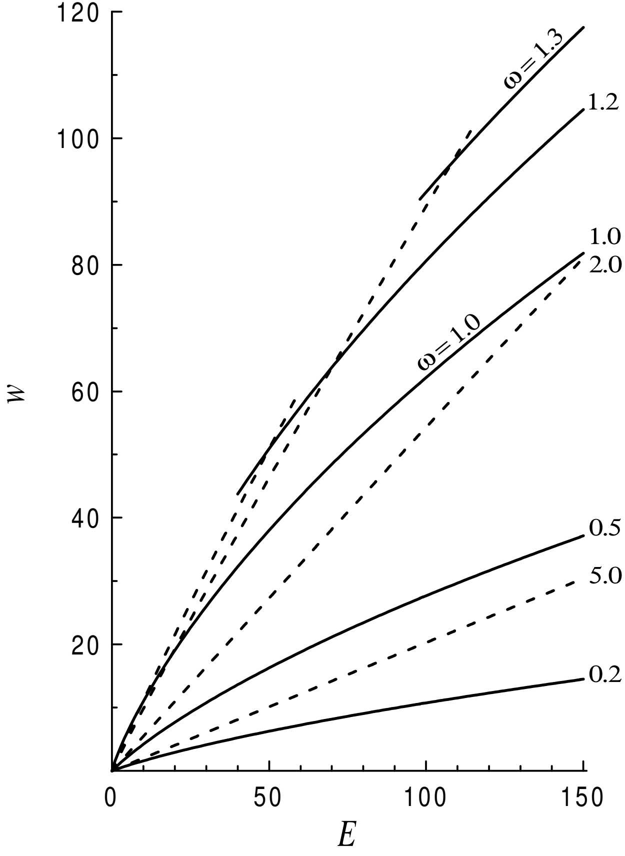


FIG. 2: Logarithm of Franck - Condon factor found in quasiclassical approximation in the limit of $\hbar \to 0$. The function $w(E)$ is the real part of the classical action. Dashed lines indicate that the action has an imaginary part as a result of analytic continuation. Compare these curves with exact quantum results for Morse oscillator shown in Fig. 1.

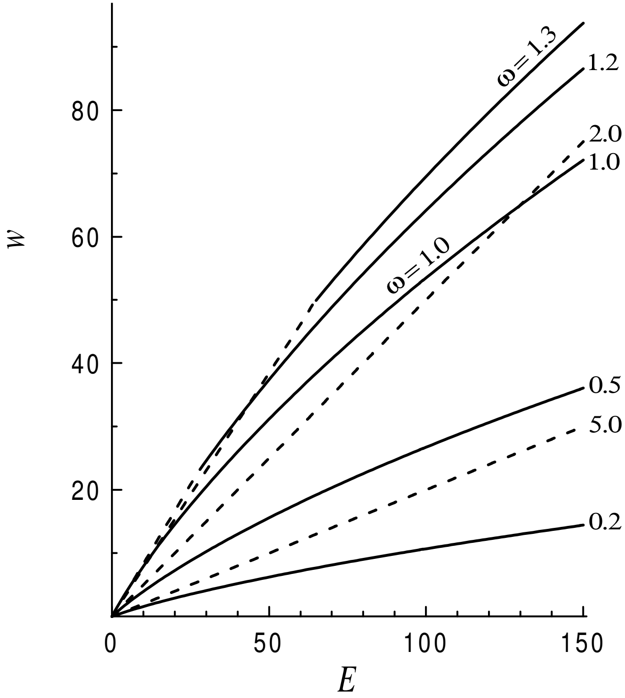


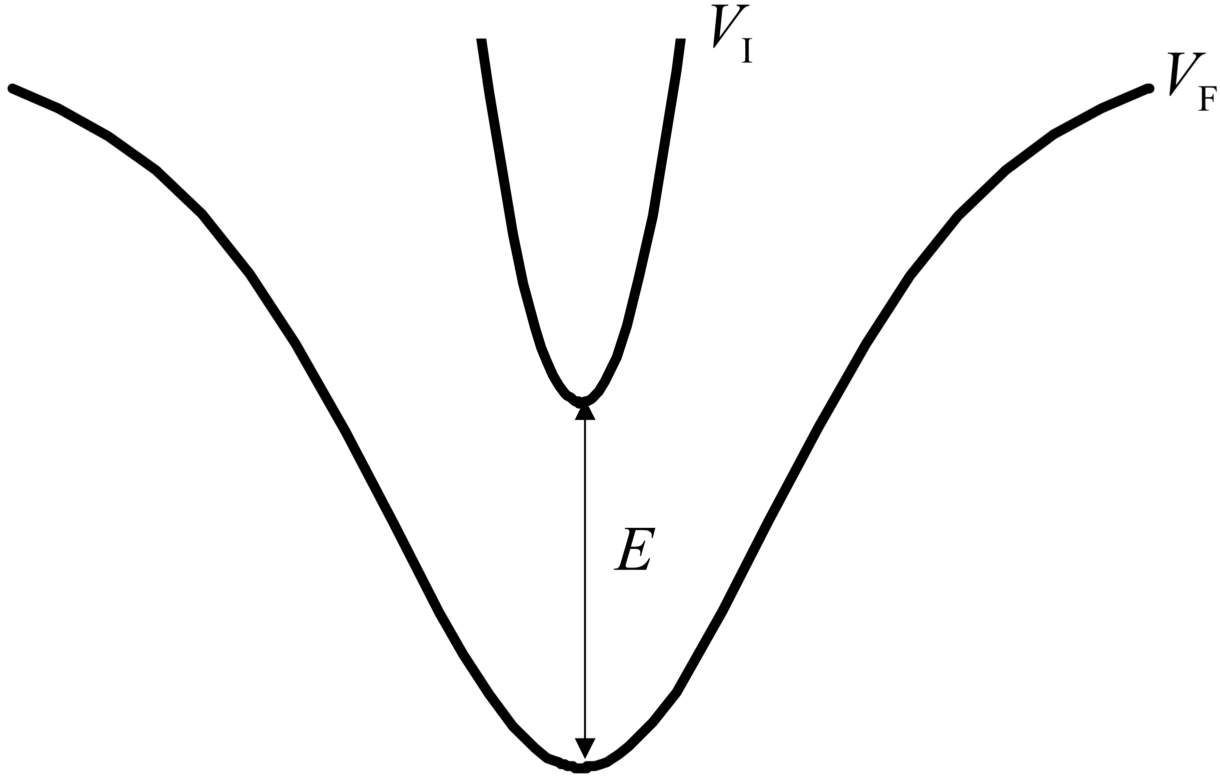
FIG. 3: Logarithm of Franck - Condon factor found by minimization of the phase space function $W(q,p)$ under the constraint $H^{(\mathrm{F})}(q,p) = E$. Dashed lines indicate that the point of minimum (q^*, p^*) has $p^* \neq 0$. Compare these curves with exact quantum results for Morse oscillator shown in Fig. 1.

Harmonic → Poeschl – Teller

$$H_{\mathrm{I}}(q,p) = \tfrac{1}{2}p^2 + \tfrac{1}{2}\omega^2 q^2$$

$$H_{\mathrm{F}}(q,p) = \tfrac{1}{2}p^2 - \tfrac{1}{2}\alpha^{-2}\left(\cosh^{-2}\alpha q - 1\right)^2$$

$$\alpha = \left[J(J+1)\right]^{-1/4}$$



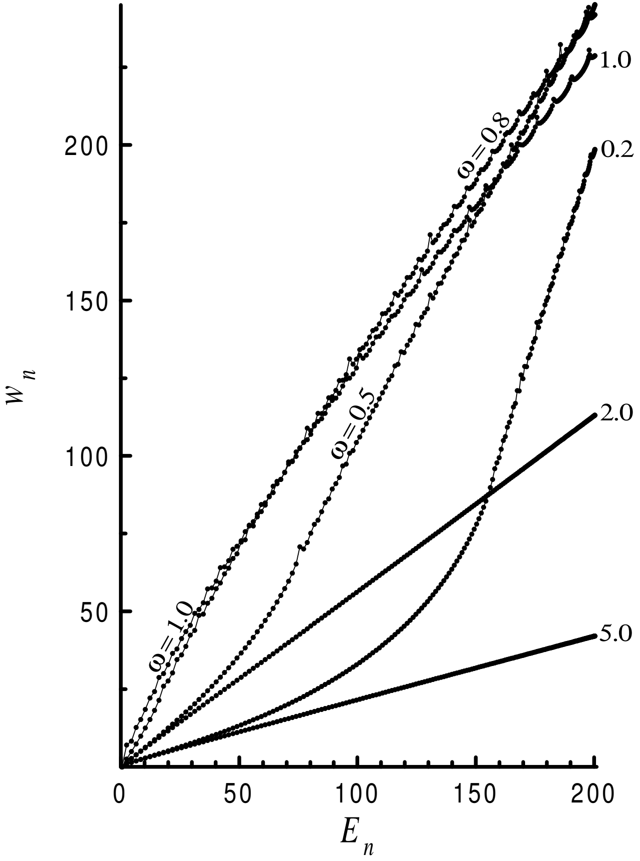


FIG. 4: Logarithm of Franck - Condon factor found by numerical integration with exact wavefunctions at the points of discrete spectrum, $E = E_n$, $n = 0, 1, \ldots, J-1$. The number of bound states is $J = 400$. Curves are labelled by values of the oscillator frequency ω.

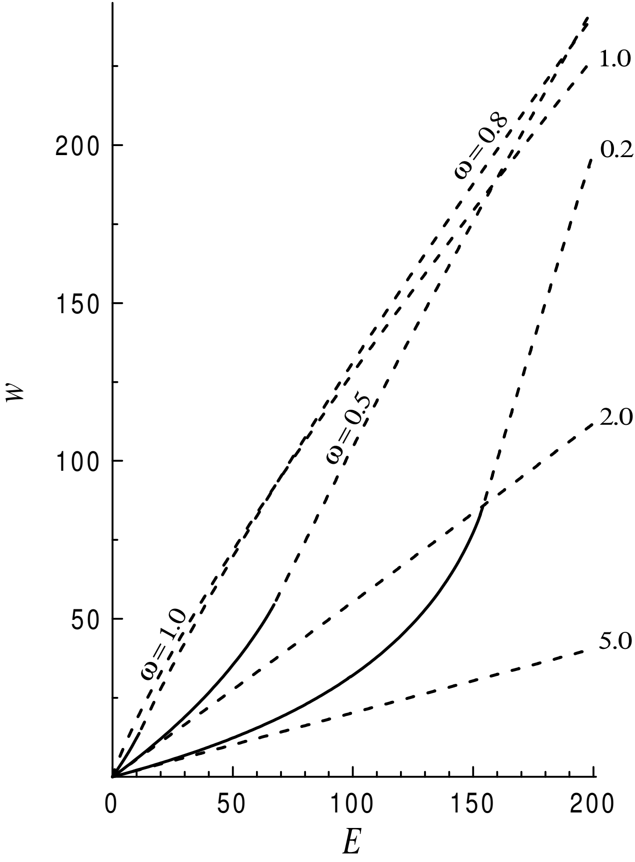


FIG. 5: Logarithm of Franck - Condon factor found in quasiclassical approximation. The function $w(E)$ is the real part of the classical action. Dashed lines indicate that the action has an imaginary part as a result of analytic continuation. Compare these curves with exact quantum results for Poeschl - Teller oscillator shown in Fig. 4.

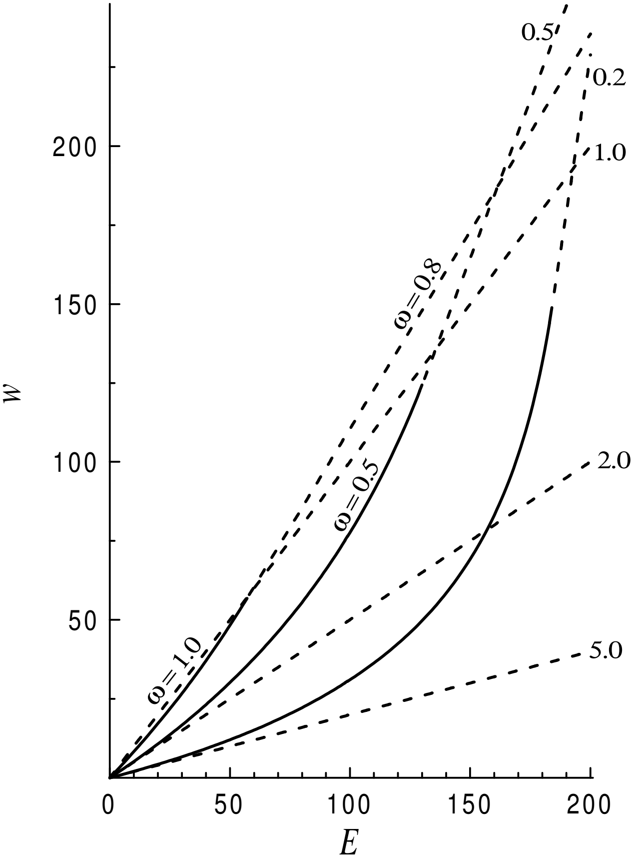


FIG. 6: Logarithm of Franck - Condon factor found by minimization of the phase space function $W(q,p)$ under the constraint $H^{(\mathrm{F})}(q,p) = E$. Dashed lines indicate that the point of minimum (q^*, p^*) has $p^* \neq 0$. Compare these curves with exact quantum results for Poeschl - Teller oscillator shown in Fig. 4.

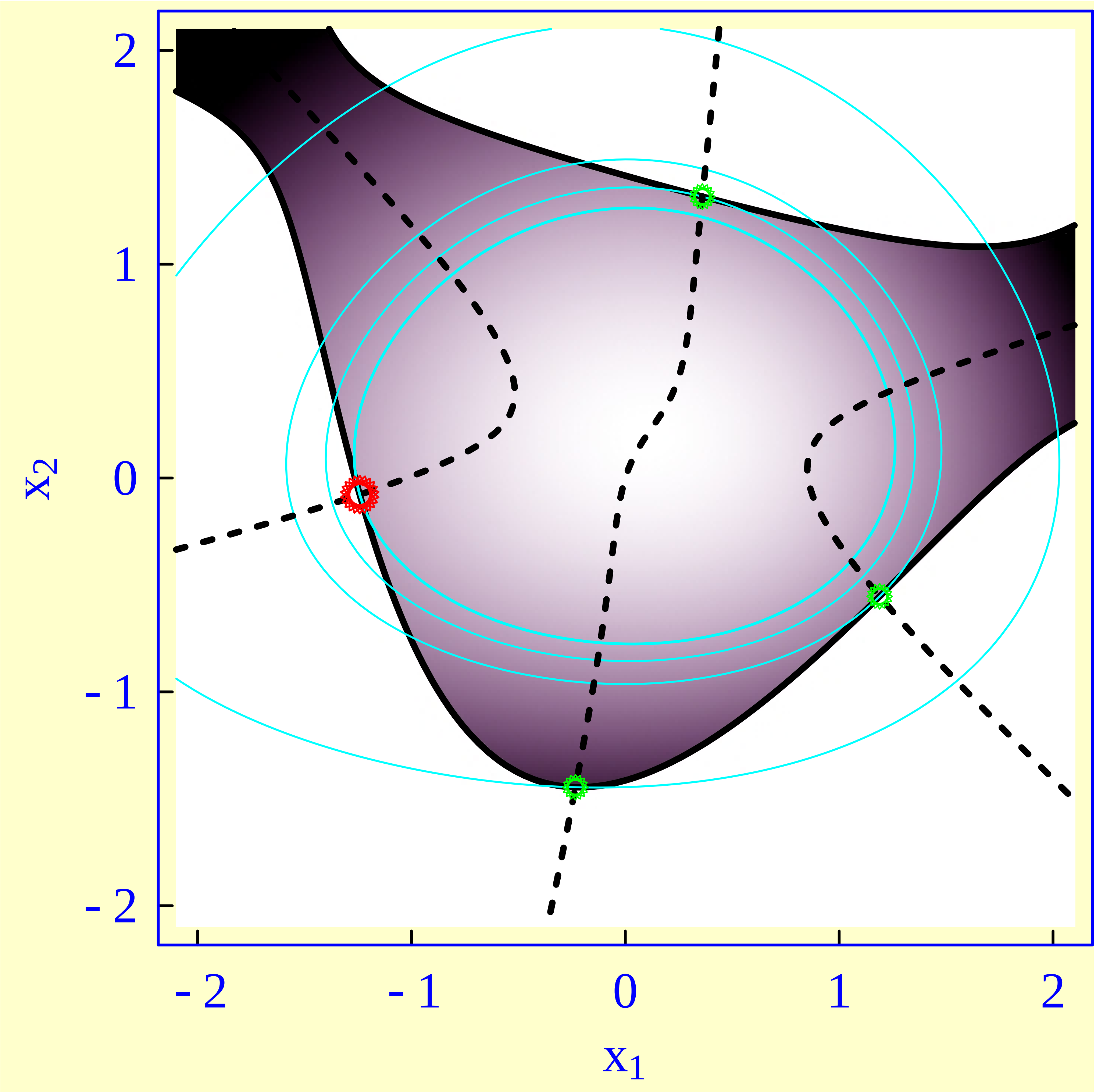


Figure 1. Finding the minimum of the function W under the energy constraint $H = E$. For this example, $W(x_1, x_2) = 0.4(x_1 - 0.1)^2 + 0.6(x_2 - 0.2)^2 + 0.05[(x_1 - 0.1)^3 + (x_1 - 0.1)^2(x_2 - 0.2) + (x_1 - 0.1)(x_2 - 0.2)^2 - (x_2 - 0.2)^3]$, $H(x_1, x_2) = \frac{1}{2}x_1^2 + \frac{1}{2}x_2^2 + 0.1[-x_1^3 - 3x_1^2 x_2 + 2x_1 x_2^2]$, and $E = 1$. Dashed lines represent stationary points of the function $F = W - \lambda H$. Energy-constraint points satisfying equation $H = E$ lie on the border of the dark area, $H < E$ (the darker is the color, the greater is the function W). Ellipses represent curves of constant W. Stationary points of the function W under the energy constraint are marked by circles. A point with the smallest W marked by a large circle is the solution of the problem: $x_1^* = -1.24$, $x_2^* = -0.08$, $W^* = 0.62$.

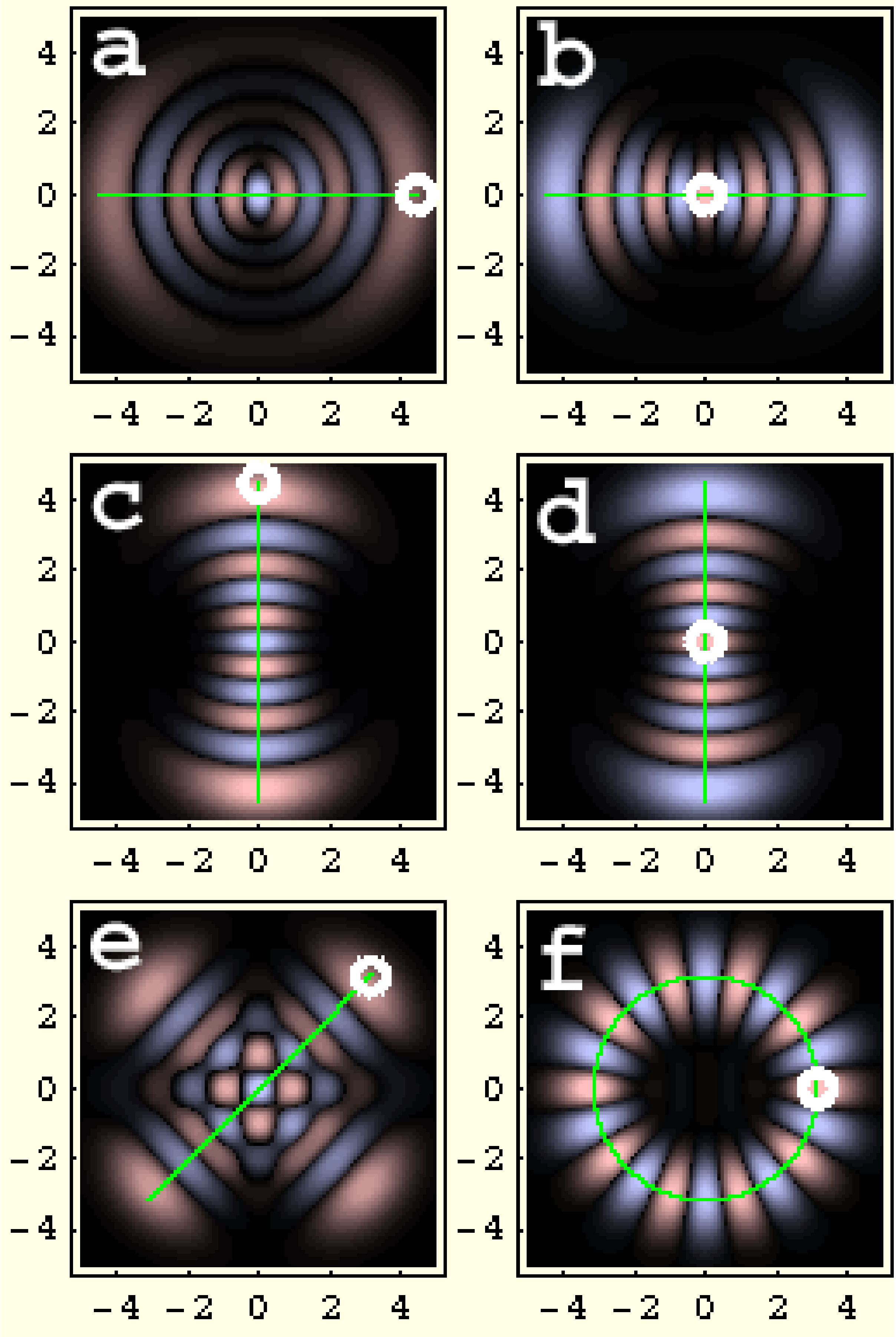


Figure 2. Pattern of the final wave function for different phase space jumps for the model of two coupled harmonic oscillators, $H_{\rm I} = \frac{1}{2}({\omega'_1}^2 p_1^2 + {\omega'_2}^2 p_2^2 + (q_1 - Q)^2 + q_2^2)$, $H_{\rm F} = \frac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2)$. The white dot marks the jumping point (q_1^*, q_2^*) that with (p_1^*, p_2^*) defines the initial conditions for the classical trajectory shown by green line or ellipse. Here, $n = 10$. The parameters ω'_1, ω'_2 and Q are the same as in the paper of Segev and Heller (2000). For the example (e), we show only one of two symmetric jumping points of equal significance.

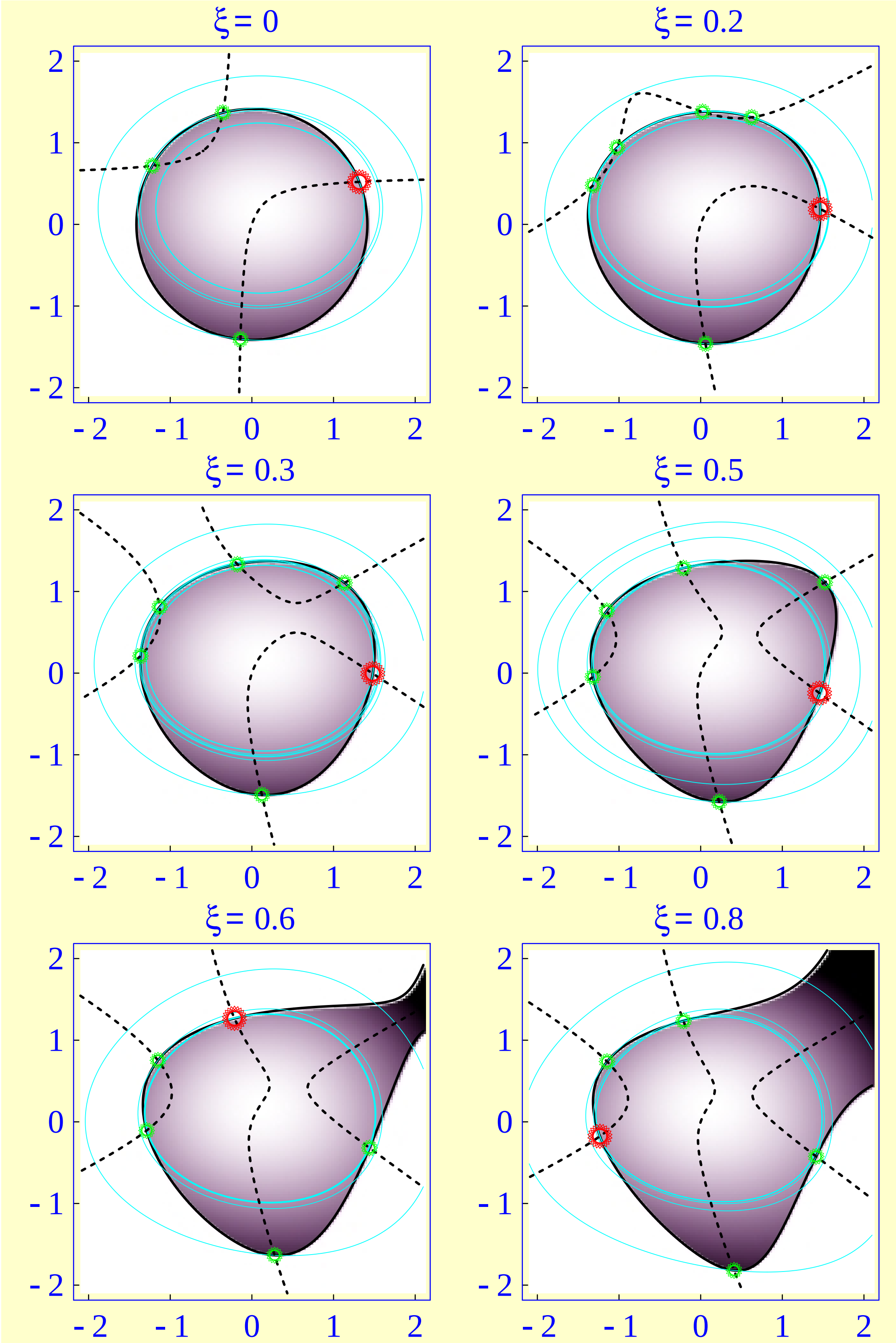


Figure 3. Evolution of the minimum of the function W under the energy constraint $H = E$ with strengthening of the anharmonicity. In W and H, we introduced an overall coupling parameter ξ: $W(x_1, x_2) = 0.4(x_1 - 0.1)^2 + 0.6(x_2 - 0.2)^2 + 0.05\xi[2(x_1 - 0.1)^2(x_2 - 0.2) - 2(x_1 - 0.1)(x_2 - 0.2)^2 + (x_2 - 0.2)^3]$, $H(x_1, x_2) = \frac{1}{2}x_1^2 + \frac{1}{2}x_2^2 + 0.1\xi[-x_1^3 - 3x_1^2x_2 - 3x_1x_2^2 + x_2^3]$, $E = 1$. The upper left corner section refers to the harmonic approximation ($\xi = 0$). Position of the global minimum marked by the largest circle is a discontinuous function of the anharmonicity since between $\xi = 0.52$ and $\xi = 0.53$ as well as between $\xi = 0.75$ and $\xi = 0.76$ the global minimum swaps with one of the secondary local minima. This example shows that for strong anharmonicities the dependence $\boldsymbol{x}^*(\xi)$ cannot be approximated by an analytic function.

References

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Acknowledgments

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