WORKSHOP ON

" QUANTUM TRAJECTORIES "

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A Bohmian Analysis of the Possible Field Induced KAM-like Transitions in Anharmonic Oscillators

P. K. Chattaraj

Department of Chemistry & Centre for Theoretical Studies

Indian Institute of Technology

Kharagpur – 721 302

India

Density Functional Theory (DFT)

Ref: [1] P. Hohenberg and W. Kohn, Phys. Rev. B 136, 864 (1964)

[2] R. G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules (Oxford Univ. Press, Oxford,1989)

$$\rho(\vec{r}) = N \int \ldots \int | \Psi(x_1, x_2, \ldots\ldots, x_N |^2 ds_1 dx_2 \ldots\ldots dx_N$$

Single particle density $\rho(\vec{r})$ is the basic variable

Hohenberg-Kohn Theorems

[1] All ground state properties of a system are unique functionals of the density.

[2] For a given external potential, the energy functional assumes a minimum value for the true density.

Euler-Lagrange Eqn:

$$\frac{\delta E[\rho]}{\delta \rho} = \mu \Rightarrow \rho(\vec{r})$$

$$\int \rho(\vec{r}) d\vec{r} = N$$

$$v(\vec{r}) \underset{\text{DFT}}{\overset{\text{SE}}{\Leftrightarrow}} \rho(\vec{r})$$

Excited- State DFT

Ref: **A. Theophilou, J. Phys. C 12, 5419 (1979)**

W. Kohn, Phys. Rev. A 34, 5419 (1986)

a) Lowest excited state of a given symmetry

b) Ensemble of states $(0 \le \omega \le 1/2)$

Quantum Fluid Dynamics (QFD)

Ref: S. K. Ghosh and B. M. Deb, Phys. Rep. 92, 1 (1982)

Motion of a probability fluid of density $\rho(\vec{r},t)$ and velocity $v(\vec{r},t)$ under the influence of the external classical potential V augumented by a quantum potential V_{qu}.

TDSE: $$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad [1] \qquad i=\sqrt{-1}$$

For a single particle of mass m in an external potential V,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$$

Polar form of the wave function:

$$\Psi = Re^{is/\hbar} \qquad [2]$$

$$R=\rho^{1/2} \quad ; \quad \vec{v}=\frac{\nabla S}{m} \quad ; \quad \vec{j}=\rho\vec{v}$$

Put [2] in [1] and separate real and imaginary parts $\Rightarrow$

Eqn. of continuity:

$$\frac{\partial \rho}{\partial t} + \nabla . \vec{j} = 0 \qquad \textbf{[3a]}$$

Eqn. of motion:

$$\frac{\partial \vec{v}}{\partial t} + (\vec{v}.\nabla)\vec{v} = -\left(\frac{1}{m}\right)\nabla\left(V + V_{qu}\right) \qquad \textbf{[3b]}$$

Quantum potential, $V_{qu} = -\frac{\hbar^2}{2m}\frac{\nabla^2 R}{R}$

Soln. Of Eqns. [3] $\Rightarrow$ $\rho(\vec{r},t)$ and $\vec{v}(\vec{r},t)$

Single-particle system $\longrightarrow$ QFD in 3-D space

Many-particle system $\longrightarrow$ QFD in 3N-D configuration space

$\downarrow$

Orbital picture : TDHF : TDKS : NO's	$\longrightarrow$ **QFD in 3-D space (N- component fluid)**

*** Towards a QFD in 3-D space : Single- component electron fluid**

Time-Dependent DFT

Ref: E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984)

$\rho(\vec{r},t)$ and $j(\vec{r},t)$ are the basic variables.

$$\frac{\partial \rho}{\partial t} + \nabla . \vec{j} = 0 \qquad \text{[4a]}$$

$$\frac{\partial \vec{j}}{\partial t} = P_{\{V\}}[\rho(\vec{r},t), \vec{j}(\vec{r},t)] \qquad \text{[4b]}$$

↓ construction of approximate functional

QFD + TDDFT $\Rightarrow$ Quantum Fluid Density Functional Theory

Ref: B. M. Deb and P. K. Chattaraj, Phys. Rev. A 39, 1696 (1989)

$$\frac{\partial \rho}{\partial t} + \nabla . (\rho \nabla \xi) = 0 \qquad \text{[5a]}$$

$$\frac{\partial \xi}{\partial t} + \frac{1}{2}(\nabla \xi)^2 + \frac{\delta G[\rho]}{\delta \rho} + \int \frac{\rho(\vec{r}',t)}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{ext}(\vec{r},t) = 0 \qquad \text{[5b]}$$

↓

ξ : Velocity potential

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\vec{r},t)\right]\Phi(\vec{r},t) = i\frac{\partial\Phi(\vec{r},t)}{\partial t} \qquad \textbf{[6a]}$$

Generalized nonlinear Schrödinger Eqn.

$$v_{eff}(\vec{r},t) = \frac{\delta T_{NW}}{\delta\rho} + \frac{\delta E_{xc}}{\delta\rho} + \int\frac{\rho(\vec{r}',t)}{|\vec{r}-\vec{r}'|}d\vec{r}' + v_{ext}(\vec{r},t) \qquad \textbf{[6b]}$$

$$\Phi(\vec{r},t) = \rho(\vec{r},t)^{1/2}\exp(i\xi(\vec{r},t)); i = \sqrt{-1}$$

$$\rho(\vec{r},t) = |\Phi(\vec{r},t)|^2$$

$$\vec{j}(\vec{r},t) = \left[\Phi_{re}\nabla\Phi_{im} - \Phi_{im}\nabla\Phi_{re}\right] = \rho\nabla\xi$$

Although classical mechanics is deterministic, it was realized in the 1970s that many classical-mechanical systems (for example, a pendulum oscillating under the influence of gravity, friction, and a periodically varying driving force) show chaotic behavior for certain ranges of the systems' parameters. In a chaotic system, the motion is extraordinarily sensitive to the initial values of the particles' positions and velocities and to the forces acting, and two initial states that differ by an experimentally undetectable amount will eventually lead to very different future behavior of the system. (For example, a physicist constructed a double pendulum for which the gravitational attraction of a raindrop one mile away is sufficient to greatly change motion after two minutes of oscillations; see J. Gleick, Chaos, Viking, New York, 1987, p. 230.) Thus, because the accuracy with which one can measure the initial state is limited, prediction of the long – term behavior of a chaotic classical – mechanical system is, in practice, impossible, even though the system obeys deterministic equations.
Computer calculations indicate that the motion of the planet Pluto may be chaotic [G. J. Sussman and J. Wisdom, Science, 241, 433 (1998); Scientific American, Oct. 1988, p. 20].

Ref: Quantum Chemistry by Ira Levine

Quantum Hénon–Heiles Oscillator

(Ref: QFD of Hénon – Heiles system)

(P. K. Chattaraj and S. Sengupta, *Phys. Lett. A* 181 (1993) 225)

$$H = \frac{1}{2}(p_x^2 + p_y^2) + V_{cl}(x,y)$$

$$V_{cl}(x,y) = \frac{1}{2}(x^2 + y^2) + \lambda(x^2 y - \frac{1}{3}y^3) \quad ; \quad \lambda = 1$$

} exhibits chaos in the classical domain

$$\Downarrow$$

$$\hat{H} = -\frac{1}{2}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}) + V_{cl}(x,y)$$

$$\hat{H}\Psi = i\frac{\partial \Psi}{\partial t} \qquad (TDSE)$$

$$\Downarrow \textbf{ QFD Eqns.}$$

$$\frac{\partial R}{\partial t} = -0.5R\nabla^2\xi - \nabla R.\nabla\xi$$

$$\frac{\partial \xi}{\partial t} = \left(\frac{1}{2R}\right)\nabla^2 R - \frac{1}{2}(\nabla\xi)^2 - V_{cl}$$

Can also be obtained as following Hamilton's EOM :

$$\frac{\delta \tilde{H}[\rho,\xi]}{\delta \rho} = \frac{\partial \chi_1}{\partial t} \quad ; \quad \frac{\delta \tilde{H}[\rho,\xi]}{\delta \chi_1} = -\frac{\partial \rho}{\partial t}$$

$$\chi_1 = -\xi \quad ; \quad \tilde{H}[\rho,\xi] = \frac{1}{2}\int \rho(\nabla\xi)^2 d\tau + \frac{1}{8}\int \frac{\nabla\rho.\nabla\rho}{\rho} d\tau + \int V_{cl}\rho\, d\tau$$

Macroscopic KE $\quad$ $\mathbf{T_W}$ $\quad$ **V**

ρ & χ_1 → "Canonical Conjugate"

x & p_x are canonically conjugate (Phase space trajectory reveals classical chaos)

Least action principle:

$$\delta \int_{t_1}^{t_2} L[\rho,\xi]dt = 0$$

$$L[\rho,\xi] = \int \rho \frac{\partial \chi_1}{\partial t} d\tau - \tilde{H}[\rho,\xi]$$

Initial boundary value problem :

Solved numerically using ADI FD scheme with Dirichlet boundary conditions for R and Neumann boundary conditions for χ.

$$R(x,y,t=0) = \frac{1}{\sqrt{\pi}} e^{-\frac{1}{2}(x^2+y^2)}$$

$$\chi(x,y,t=0) = 0, \ \forall x,y$$

$$R\,(x,\pm\infty) = 0, \ \forall t,x$$

$$R\,(\pm\infty,y) = 0, \ \forall t,y$$

$$\frac{\partial \chi}{\partial x}\,(\pm\infty,y) = 0, \ \forall t,y$$

$$\frac{\partial \chi}{\partial y}\,(x,\pm\infty) = 0, \ \forall t,x$$

$\lambda = 0\ (linear)\ ;\ 0.1;\ 0.19$

$\Delta x = \Delta y = 0.2, \ \Delta t = 0.0065 \Rightarrow$ forward – time – central – space - type FDS stable

TO follow the dynamics calculate :

(a) Shannon entropy :

$$S = -k\int \rho \ln \rho \, d\tau$$

(b) density correlation :

$$C = 2\pi\int \rho(0)\rho(t)\, d\tau$$

(c) macroscopic KE :

$$T = \frac{1}{2}\int \rho(\nabla\chi)^2 \, d\tau$$

ρ vs. (-χ) plots ; t=100, 150

Ref: P. K. Chattaraj and S. Sengupta, *Phys. Lett. A* 181 (1993) 225.

Quantum Theory of Motion (QTM): de Bröglie-Bohm representation

Ref: P. R. Holland, The quantum theory of motion
(Cambridge Univ. Press, Cambridge, 1993).

Motion of a particle experiencing forces originating from both classical and quantum potentials.

Newton's EOM for the particle:

$$(\frac{\partial}{\partial t} + \dot{\vec{r}}.\nabla)(m\dot{\vec{r}}) = -\nabla\left(V + V_{qu}\right)|_{\vec{r}=\vec{r}(t)} \qquad \ldots \quad (1)$$

Basic postulates of QTM

Ref: D. Bohm, *Phys. Rev.* 85 (1952) 166, 180
P. R. Holland's book.

a) "An individual physical system comprises a wave propagating in space and time together with a point particle which moves continuously under the guidance of the wave".

b) "The wave is mathematically described by $\Psi(\vec{r},t)$, a solution to TDSE".

c) "The particle motion is obtained as the solution $\vec{r}(t)$ to the equation

$$\vec{v} = \dot{\vec{r}} = (\frac{1}{m})\nabla S(\vec{r},t)\,|_{\vec{r}=\vec{r}(t)} \qquad \ldots \quad (2)$$

To solve this eqn. we have to specify the initial condition $\vec{r}(0) = \vec{r}_0$. This specification constitutes the only extra information introduced by the theory that is not contained in $\Psi(\vec{r},t)$. An ensemble of possible motions associated with the same wave is generated by varying $\vec{r}_0$. Choice of $\vec{r}_0$ is arbitrary except that it cannot lie in a nodal region, since at these points ∇s_0 is undefined.

(d) "The probability that a particle in the ensemble lies between $\vec{r}$ and $\vec{r} + d\vec{r}$ at time t is given by $\rho(\vec{r},t)d\vec{r}$ where $\rho(\vec{r},t) = |\Psi|^2$ ".

QTM of Hénon – Heiles System :

S. Sengupta & P. K. Chattaraj, *Phys. Lett. A* 215 (1996) 119.

Quantum Theory of motion of a Hénon-Heiles Oscillator

TDSE :

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad \ldots \quad (1)$$

$$V = \frac{1}{2}(x^2 + y^2) + \lambda(x^2 y - \frac{1}{3}y^3)$$

Eq. (1) is solved numerically using a Peaceman – Rachford type FDA :

$$\Psi(x, y; t + \Delta t) = \exp(-i\hat{H}\Delta t)\Psi(x, y; t)$$

Velocity eqn:

$$\dot{\vec{r}} = \frac{\nabla S(\vec{r}, t)}{m} = \mathrm{Re}\left[-\frac{i\hbar\nabla\Psi}{m\Psi}\right]$$

— Solved using a second order Runge – Kutta method.

Initial & Boundary Conditions:

$$\Psi(x, y; t = 0) = \left(\frac{1}{\sqrt{2\pi}}\right)^{\frac{1}{2}} \exp\left\{-\frac{1}{2\sqrt{2}}[(x - x_0)^2 + (y - y_0)^2]\right\}$$

$$\Psi(\pm\infty, y; t) = 0 \qquad \forall\ y, t$$

$$\Psi(x, \pm\infty; t) = 0 \qquad \forall\ x, t$$

Quantities Calculated :

(i) Distance function :

$$D(t) = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (p_{x_1} - p_{x_2})^2 + (p_{y_1} - p_{y_2})^2}$$

(ii) Quantum Lyapunov exponent :

$$\Lambda = \underset{\substack{D(0)\to 0 \\ t\to\infty}}{Lt} \frac{1}{t} \ln\left[\frac{D(t)}{D(0)}\right]$$

(iii) Kolmogorov – Sinai entropy :

$$H = \sum_{\Lambda_+ \succ 0} \Lambda_+$$

(iv) de – Broglie wave length :

$$\lambda = \frac{2\pi}{|\dot{\vec{r}}|}$$

Ref: S. Sengupta and P. K. Chattaraj, *Phys. Lett. A* 215 (1996) 119.

Chaotic dynamics of some quantum anharmonic oscillators

$$V(x,y) = \frac{1}{2}(Ax^2 + By^2) + \lambda(Cx^2 y + \frac{D}{3} y^3)$$

(a) Harmonic : A=B=1, λ=0

(b) Hénon – Heiles : λ≠0, A=B=C=1, D=-1

(c) Barbanis : λ≠0, A=B=C=1, D=0

(d) Chang – Tabor - Weiss : λ≠0, A=C=1, B=D=16 (Integrable)

Quantities Calculated:

(i) Phase space distance function

(ii) Quantum Lyapunov exponent

(iii) Kolmogorov – Sinai entropy

(iv) Standard diagnostics :

a) Autocorrelation function & its power spectrum

b) Nearest neighbour spacing distribution

c) Spectral rigidity

d) Phase space volume, $\mathbf{V_{ps}}$

$$V_{ps} = [\langle (x - \langle x \rangle)^2 \rangle \langle (p_x - \langle p_x \rangle)^2 \rangle \langle (y - \langle y \rangle)^2 \rangle \langle (p_y - \langle p_y \rangle)^2 \rangle]^{1/2}$$

Ref: (1) P. K. Chattaraj, S. Sengupta and A. Poddar, *Ind. J. Chem. A* 39 (2000) 316.

(2) — , *Curr. Sci.* 74 (1998) 758.

(3) — , *Int. J. Quantum Chem., DFT Spl. Issue*, 69 (1998) 279.

(4) — , in "Nonlinear Dynamics and Computational Physics", (Ed.), V. B. Sheorey, Narosa, New Delhi, 1999, pp.45- 53.

(5) — , in "Nonlinear Dynamics : Integrability and Chaos", (Ed.), M. Daniel, K. M. Tamizhmani and R. Sahadevan, Narosa, New Delhi, 2000, pp. 287-298.

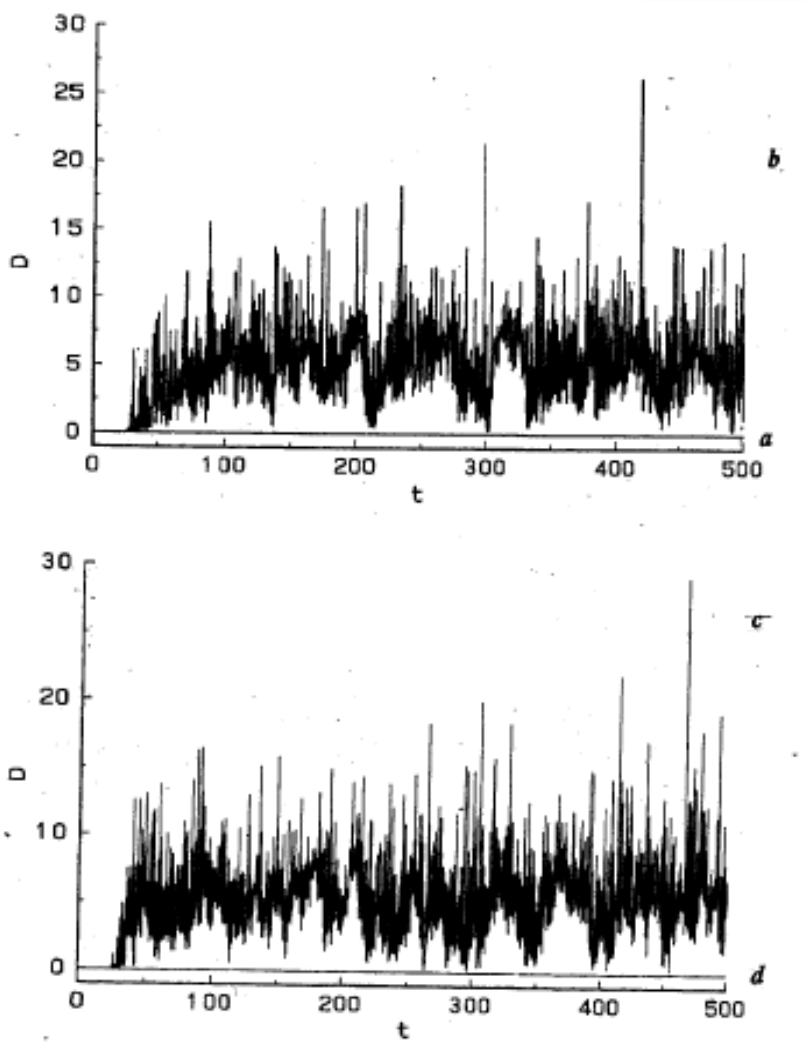


Figure 1. Time evolution of phase space distance, D for (a) harmonic oscillator with $x_0 = 1.36719$, $y_0 = 1.36719$, (b) Hénon–Heiles oscillator, with $\lambda = 0.1118034$ and $x_0 = 1.36719$, $y_0 = 1.36719$, (c) Barbanis oscillator, with $\lambda = 0.1118034$ and $x_0 = 2.929688$, $y_0 = 1.953125$, (d) CTW oscillator, $\lambda = 0.1118034$ and $x_0 = 1.25$, $y_0 = 0.5$. Figures *a* and *b* are presented together as is the case with Figures *c* and *d*.

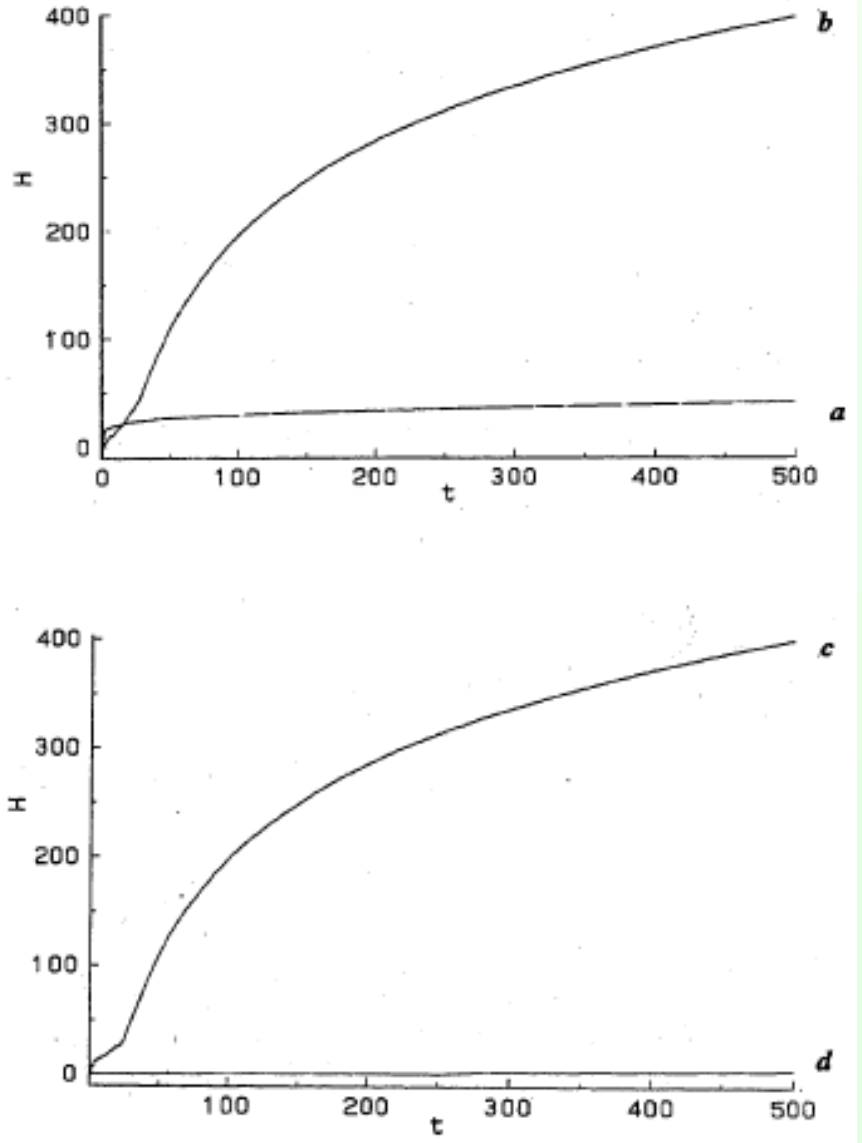
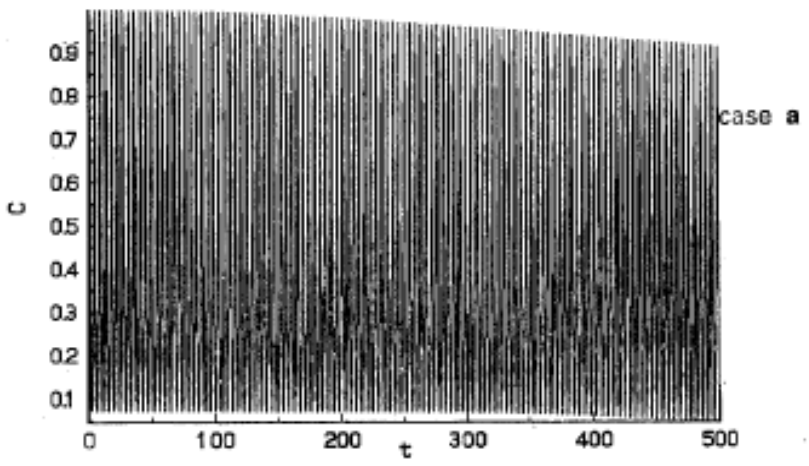


Figure 2. Time evolution of KS entropy, H for cases *a*–*d*. Figures *a* and *b* are presented together as is the case with Figures *c* and *d*.

P. K. CHATTARAJ, S. SENGUPTA & A. PODDAR, *CURR. SCI.* 74 (1998) 758.



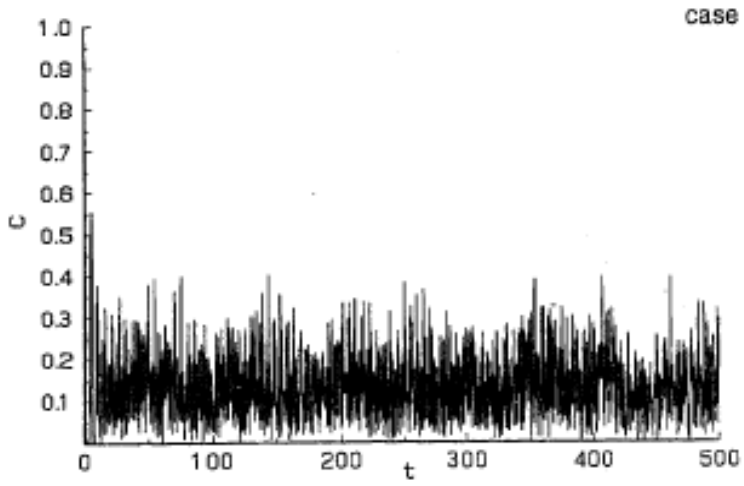
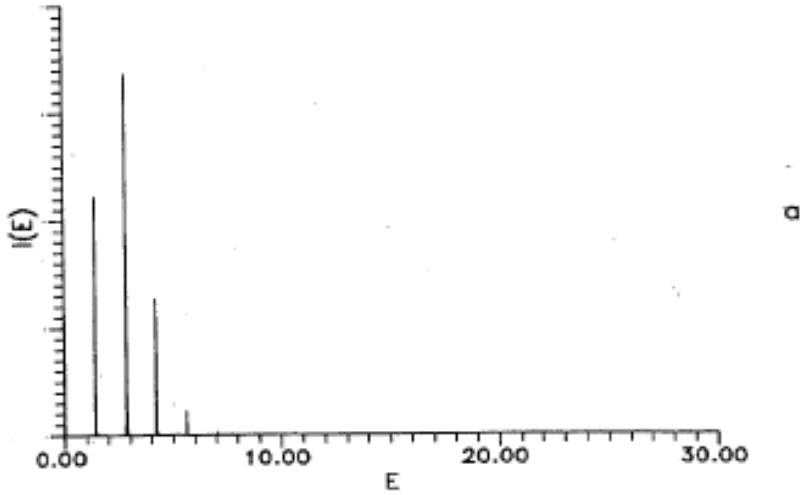


Figure 3. Time evolution of autocorrelation, C for cases a and c.



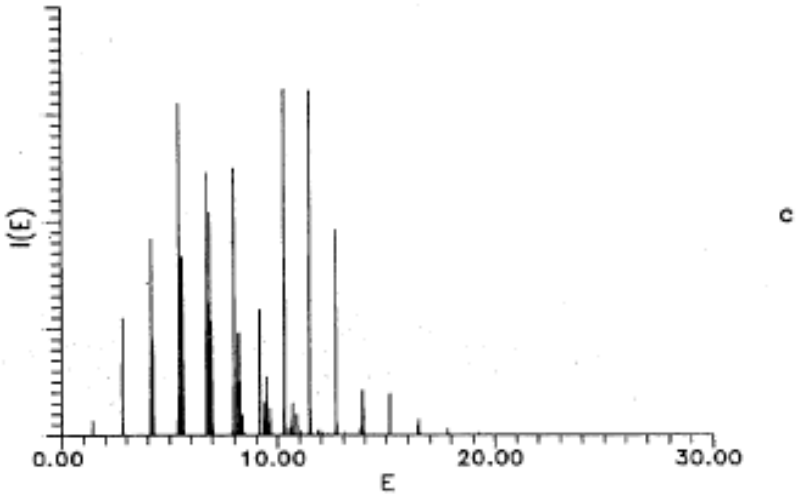


Figure 4. Power spectra, I(E) for cases a and c.

P. K. CHATTARAJ, S. SENGUPTA & A. PODDAR, *CURR. SCI.* 74 (1998) 758.

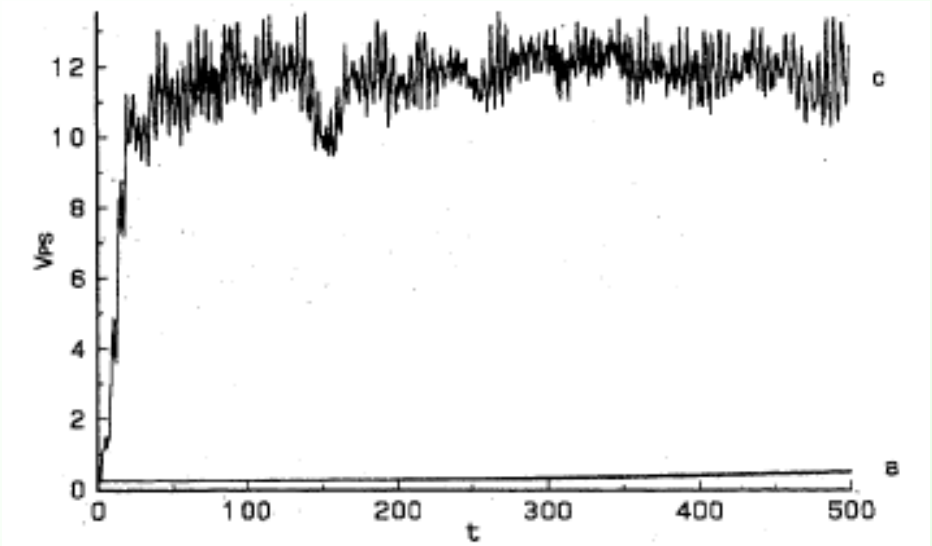


Figure 5. Time evolution of phase space volume, V_{ps} for cases a and c.

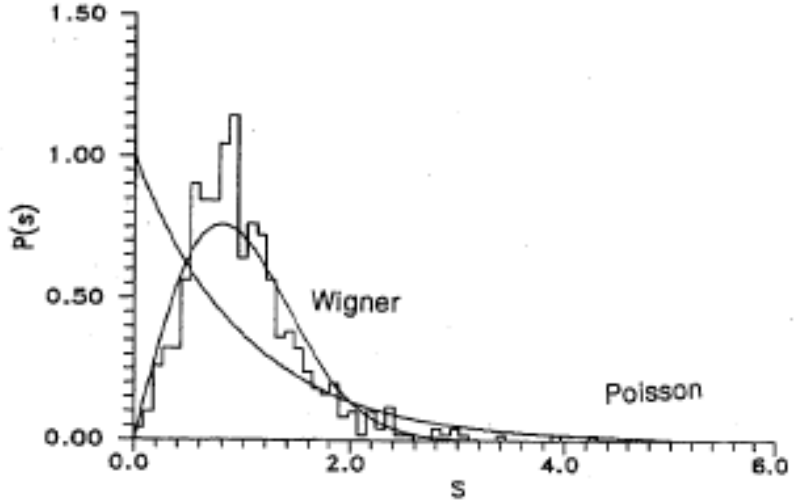


Figure 6. Nearest-neighbour spacing distribution, $P(s)$ as a function of the spacing between consecutive energy levels s. Only case **c** is presented.

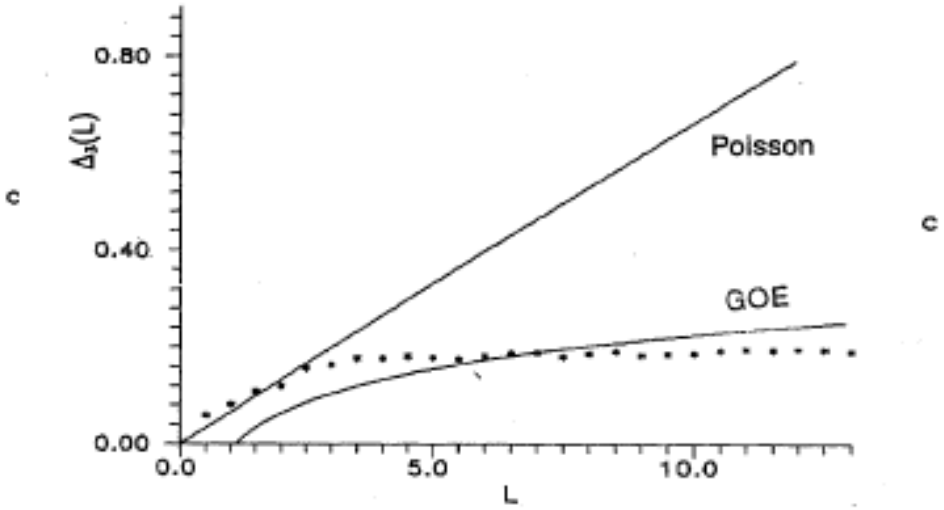


Figure 7. Spectral rigidity, $\Delta_3(L)$ as a function of energy interval L. Only case **c** is presented.

P. K. CHATTARAJ, S. SENGUPTA & A. PODDAR, *CURR. SCI.* 74 (1998) 758.

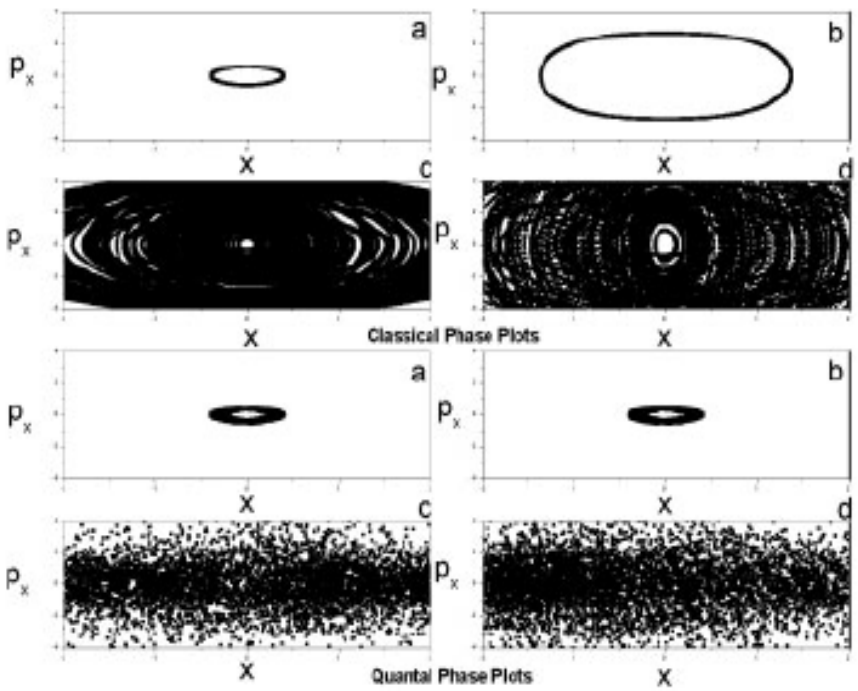


FIGURE 39. Classical and quantal phase space trajectories. For case a: $x_o = 0.390625$, $y_o = 0.390625$, $p_{x_0} = 0.0$ and $p_{y_0} = 0.0$; case b: $x_o = 1.36719$, $y_o = 1.36719$, $p_{x_0} = 0.0$ and $p_{y_0} = 0.0$; case c: $x_o = 2.34375$, $y_o = 0.0$, $p_{x_0} = 0.0$ and $p_{y_0} = 2.91358$; case d: $x_o = 2.929688$, $y_o = 1.953125$, $p_{x_0} = 0.0$ and $p_{y_0} = 0.0$.

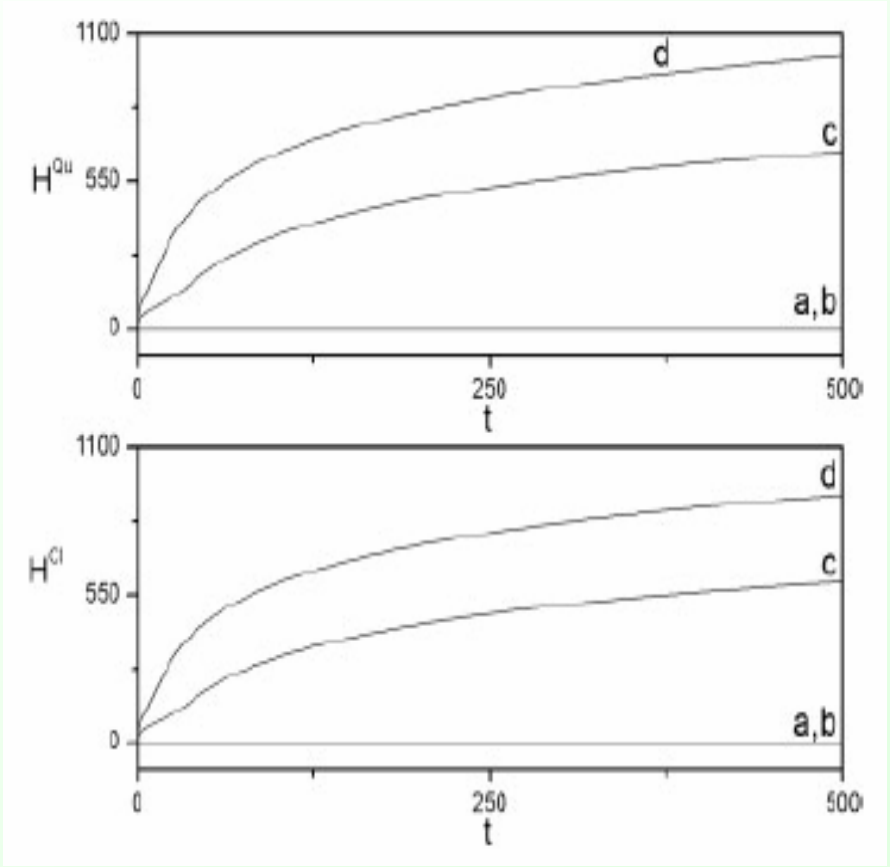


FIGURE 40. Time evolution of classical (H^{Cl}) and quantal (H^{Qu}) KSL entropies.

$$H(x,y) = \frac{1}{2}(p_x^2 + p_y^2) + A(x^2 + y^2) + Bx^2y^2$$

$$A = 0.5 \quad , \quad B = 0.118034$$

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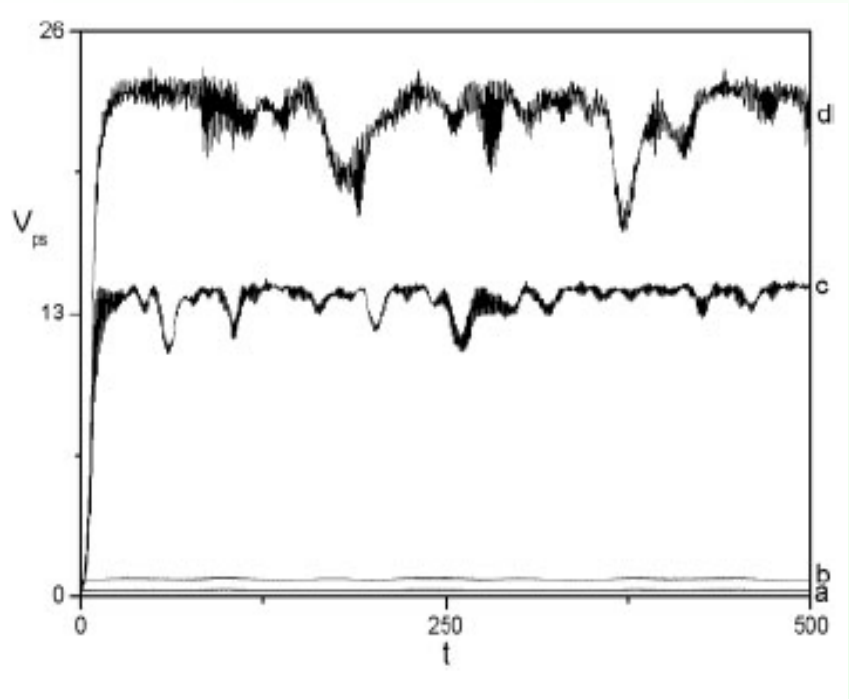


FIGURE 41. Time evolution of phase space volume (V_{ps}) or uncertainty product associated with the quantal motion.

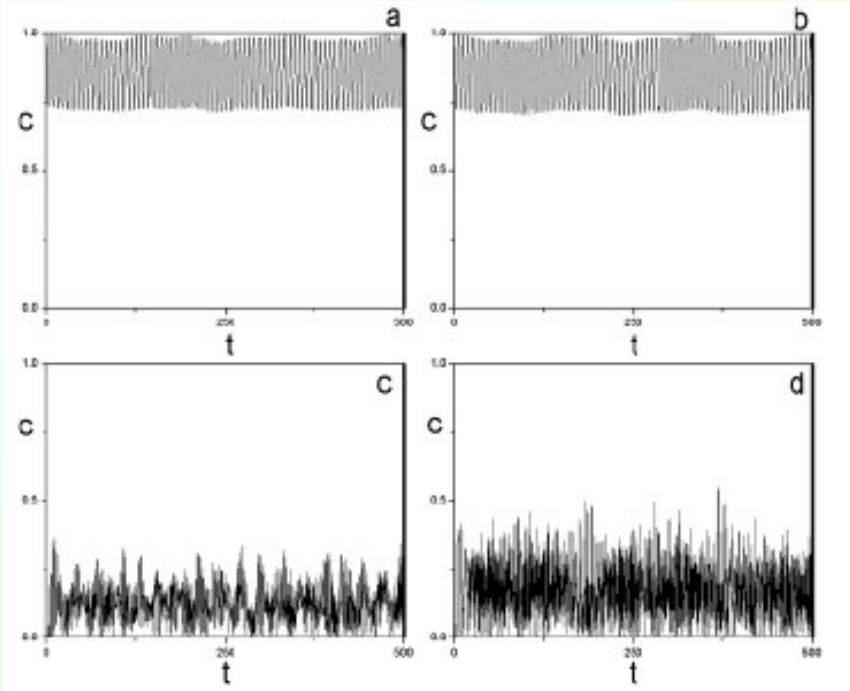


FIGURE 42. Time evolution of autocorrelation, *c* for cases a, b, c and d.

P. K. CHATTARAJ, B. MAITI & S. SENGUPTA, *INT. J. QUANTUM CHEM.* 100 (2004) 254.

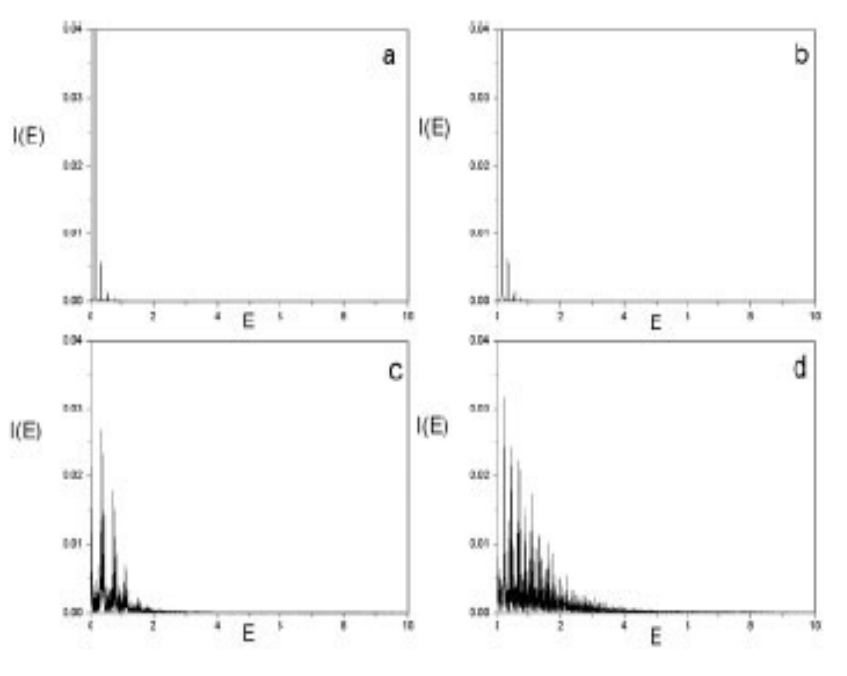


FIGURE 43. Power spectra, $I(E)$ for cases a, b, c, and d.

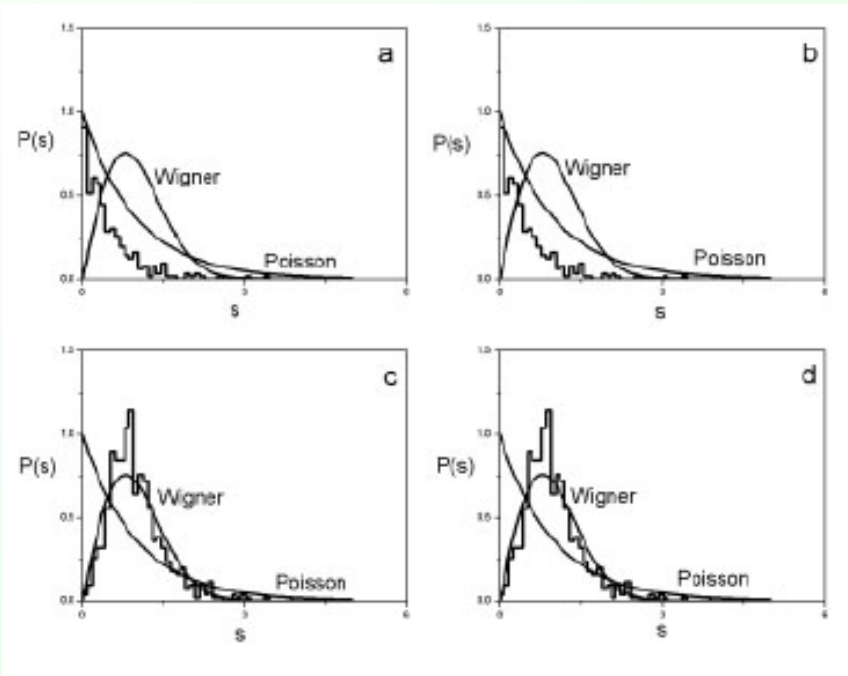


FIGURE 44. Nearest—neighbor spacing distribution, $P(s)$ as a function of the spacing between consecutive energy levels s for cases a, b, c and d.

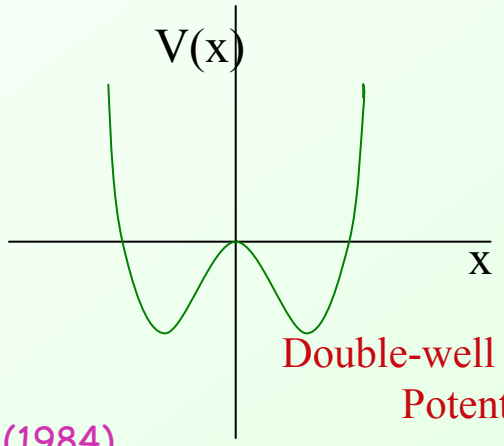
P. K. CHATTARAJ, B. MAITI & S. SENGUPTA, *INT. J. QUANTUM CHEM.* 100 (2004) 254.

Field-induced Quantum Tunneling : A QTM study

Ref: P. K. Chattaraj, S. Sengupta and A. Poddar, *Curr. Sci.* 76 (1999) 1371.

$$H = \frac{p^2}{2m} + V(x) + \gamma x \cos(\omega t)$$

$$V(x) = \alpha x^4 - \beta x^2$$



Double-well (Quartic) Potential

Ref: (1) W. A. Lin and L. E. Ballentine, Phys. Rev. Lett. 65 , 2927 (1990).

$m = 1, \alpha = 0.5, \beta = 10, \gamma = 10, \omega = 6.07$

(2) L. E. Reichl and W. M. Zhang, Phys. Rev. A 29 , 2186 (1984).

(3) S. Chaudhuri, G. Gangopadhyay and D. S. Ray, Indian J. Phys. 69B , 507 (1995).

Four Cases :

Classical Dynamics	Initial (t=0) Phase – space Variables (x_0, p_0)	Symbol
a) Regular	(-2.0 , 0.0)	◇
b) Regular	(-1.468 , 0.0)	⬭
c) Chaotic	(1.85 , 0.0)	* * *
d) Chaotic	(2.0 , 0.0)	• • •

Cases a) & d) $\Rightarrow$ Same energy ($E_0^{Cl} = -32$) : unperturbed system

Classical Hamilton's EOM $\Rightarrow$ 4th order Runge – Kutta

$\Delta x|_{t=0} = 10^{-5}$; KS – entropy formula : as before

QTM Aspects :

Case one : $\lambda = 1$

$$\hat{H} = -\frac{1}{2}\frac{d^2}{dx^2} + \lambda[V(x) + \gamma\, x\cos(\omega t)] \quad : \hbar = 1$$

Quantum versions of cases a – d.

Case two : $\lambda \neq 1$

$$\lambda = \frac{(V_{cl})\,|_{t=0,\gamma=0}}{\langle V\rangle_{qu}\,|_{t=0,\gamma=0}}$$ (Generally close to unity)

$$\Psi(x, t=0) = \left(\frac{1}{\pi}\right)^{\frac{1}{4}} e^{(x-x_0)^2/2} \quad ; \quad -9.5 \le x \le 9.5 \quad ; \quad dx = 0.1,\ dt = 0.02$$

$$\Delta x\,|_{t=0} = 10^{-5} \quad \text{in all cases}$$

Numerical algorithm : Same as before (Q. anharmonic oscillators)

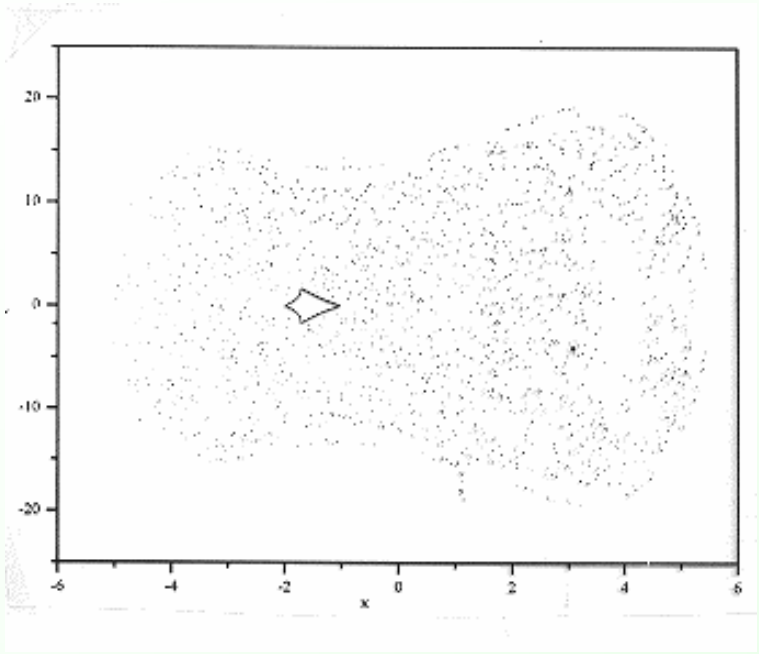


Figure 1. Classical phase space trajectories for a double-well oscillator in the presence of an external field with c = 10 and two different initial conditions: (a) (x_0 = –2.0, p_0 = 0.0); (b) (x_0 = 2.0, p_0 = 0.0).

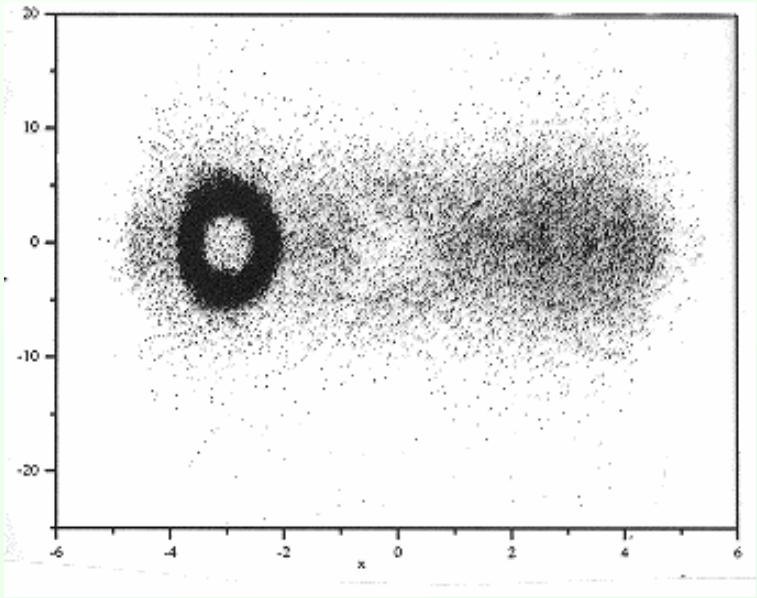


Figure 2. Quantal phase space trajectories for a double-well oscillator in the presence of an external field with c = 10 and two different initial conditions: (a) (x_0 = –2.0, p_0 = 0.0); (b) (x_0 = 2.0, p_0 = 0.0).

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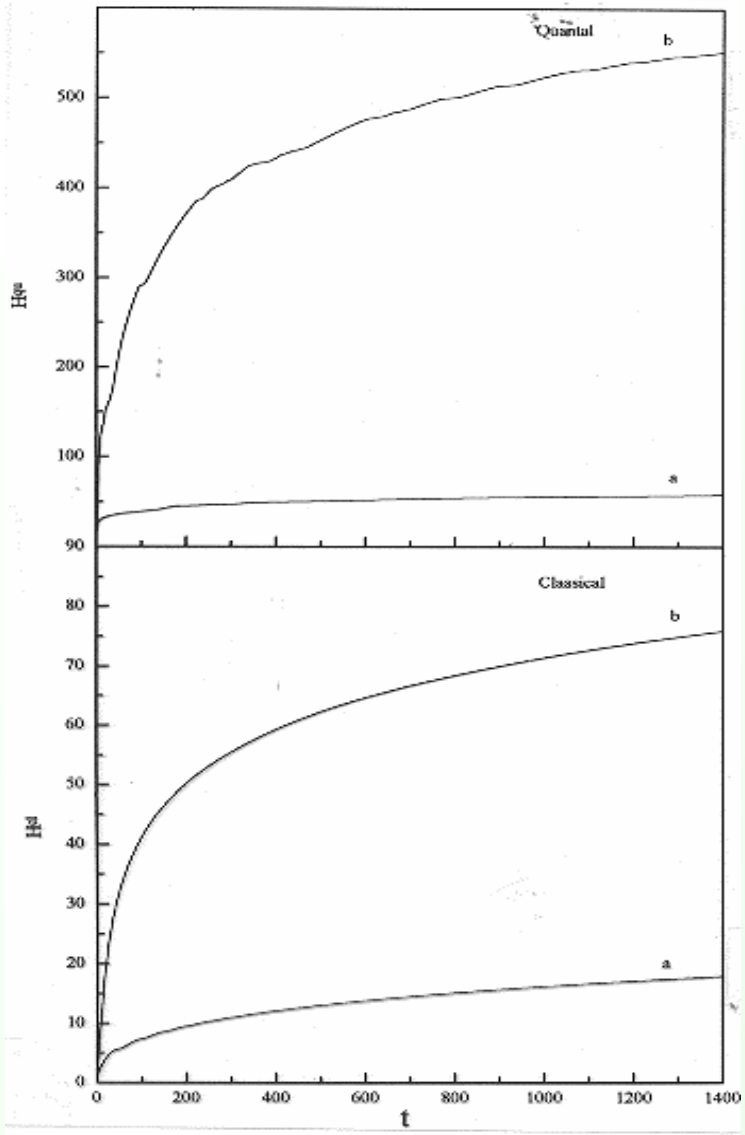


Figure 3. Time evolution of the KS entropy associated with the classical motion (H^{cl}) and quantal motion (H^{qu}) for a double-well oscillator in the presence of an external field with c = 10 and two different initial conditions:
(a) (x_0 = -2.0, p_0 = 0.0); (b) (x_0 = 2.0, p_0 = 0.0).

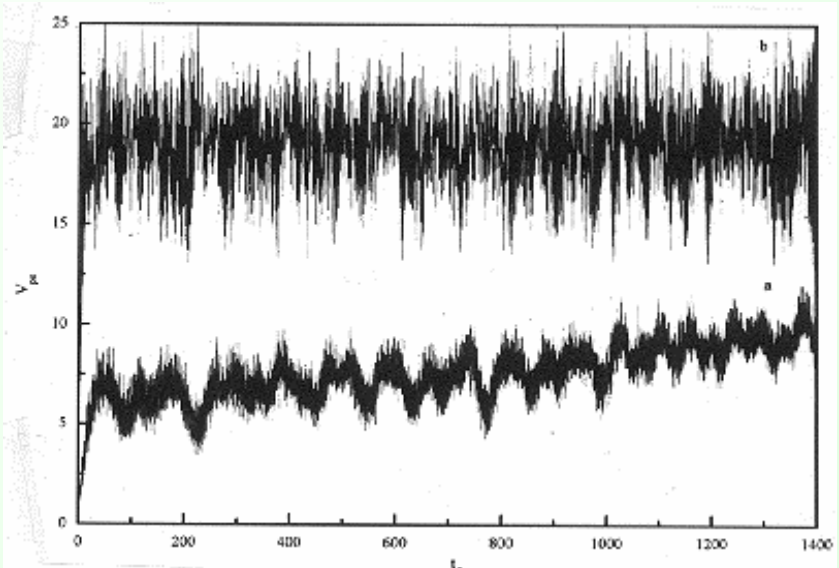


Figure 4. Time evolution of the phase space volume V_{ps} associated with the quantal motion for a double-well oscillator in the presence of an external field with c = 10 and two different initial conditions:
(a) (x_0 = –2.0, p_0 = 0.0); (b) (x_0 = 2.0, p_0 = 0.0).

P. K. CHATTARAJ, S. SENGUPTA & A. PODDAR, *CURR. SCI.* 76 (1999) 1371.

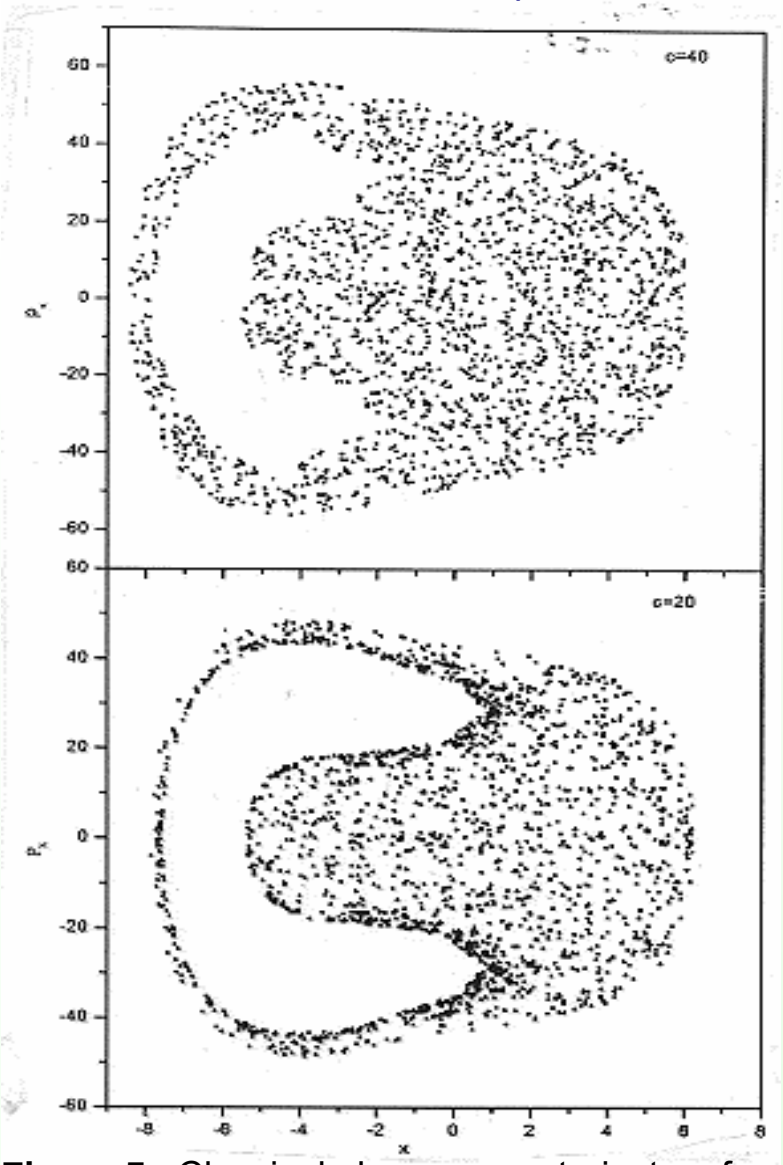


Figure 5. Classical phase space trajectory for a double-well oscillator in the presence of an external field with c = 20 and c = 40 with initial condition: (x_0 = –2.0, p_0 = 0.0).

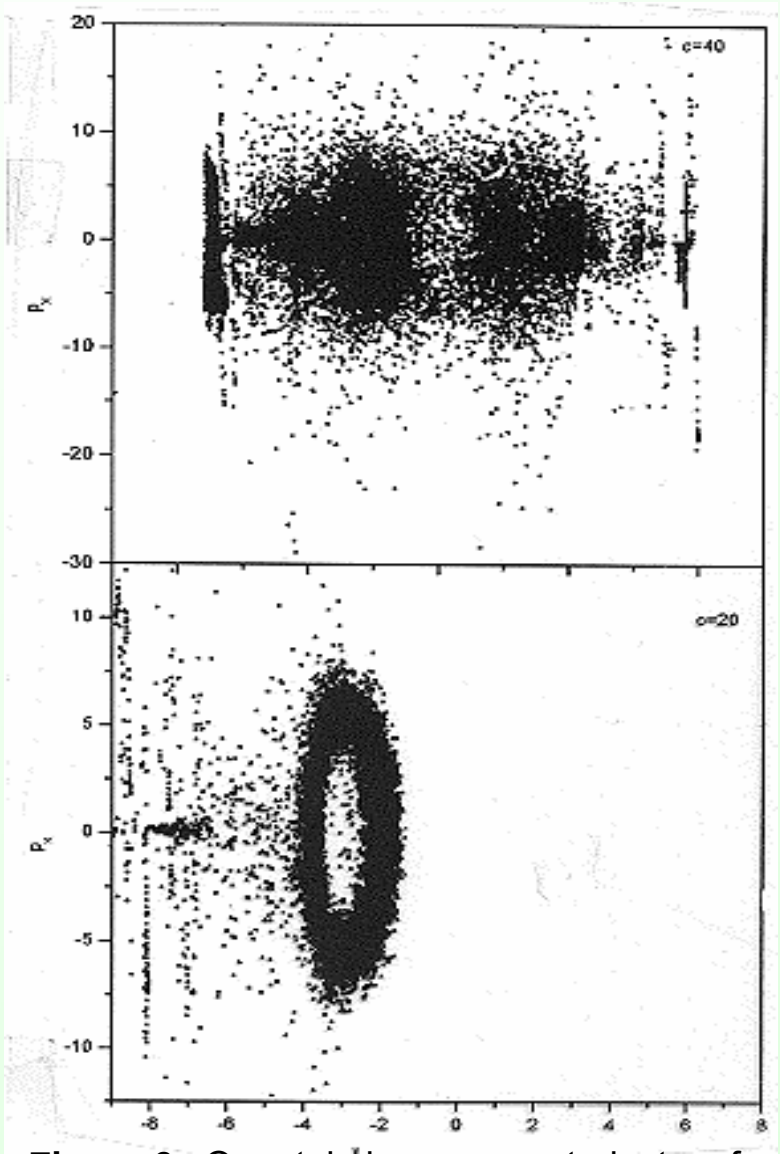


Figure 6. Quantal phase space trajectory for a double-well oscillator in the presence of an external field with c = 20 and c = 40 with initial condition: (x_0 = –2.0, p_0 = 0.0).

P. K. CHATTARAJ, S. SENGUPTA & A. PODDAR, *CURR. SCI.* 76 (1999) 1371.

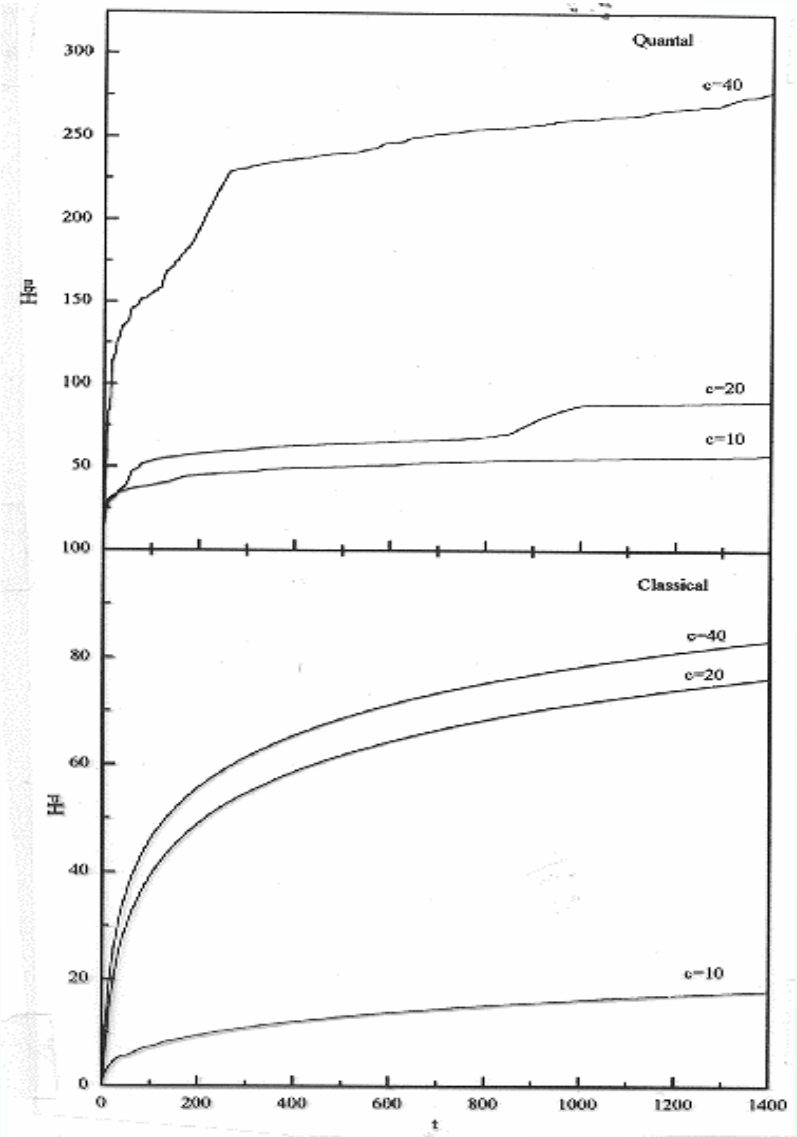


Figure 7. Time evolution of the KS entropy associated with the classical motion (H^{cl}) and quantal motion (H^{qu}) for a double-well oscillator in the presence of an external field with c = 10, 20 and 40 respectively, with initial condition: (x_0 = –2.0, p_0 = 0.0).

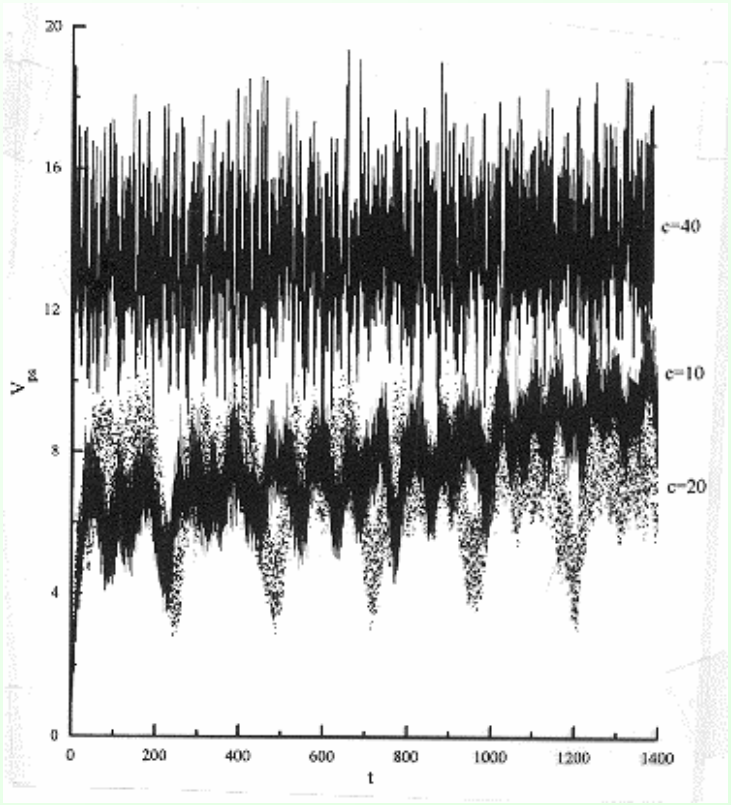
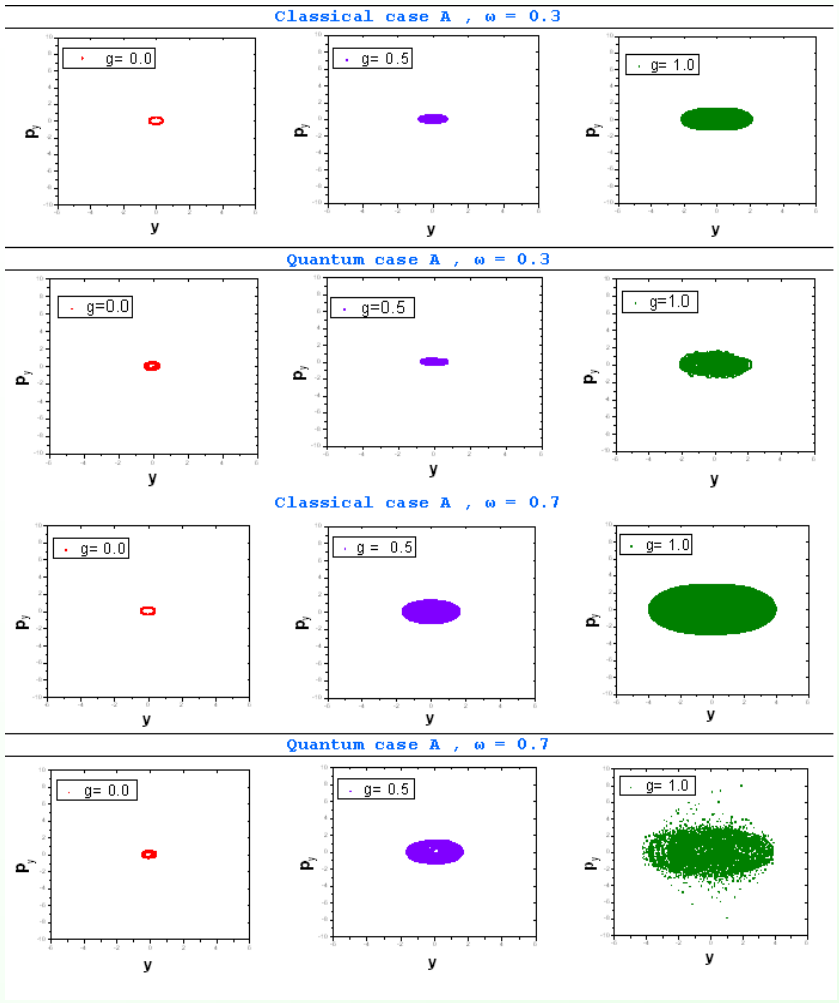
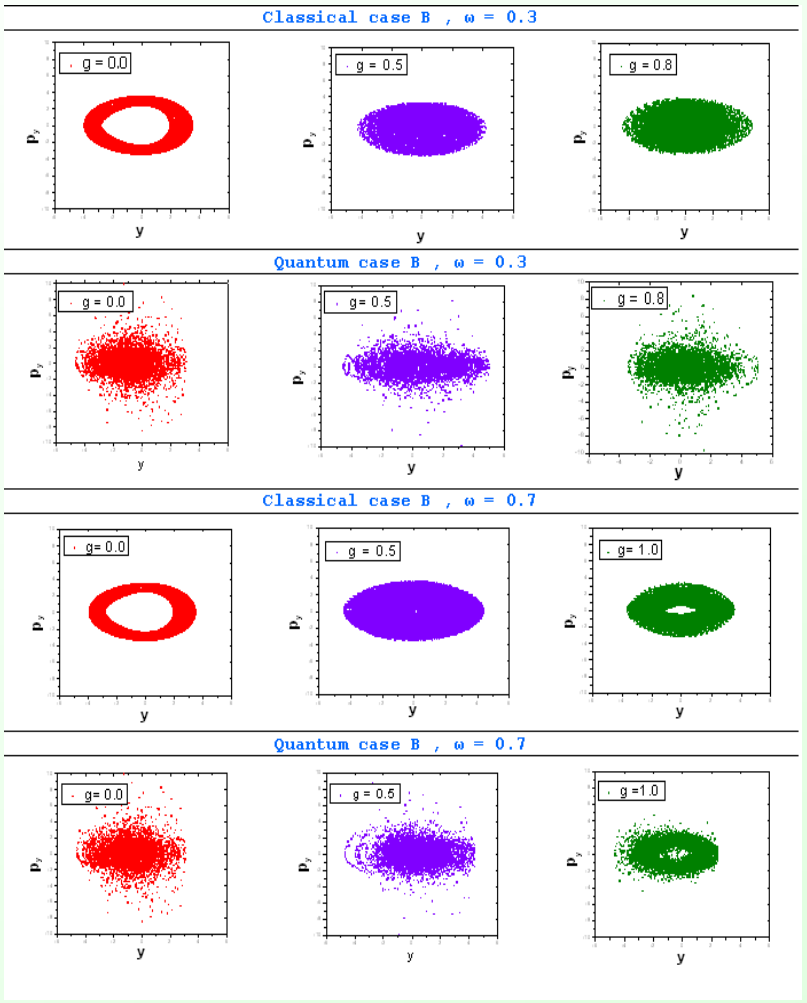


Figure 8. Time evolution of the phase space volume V_{ps} associated with the quantal motion for a double-well oscillator in the presence of an external field with c = 10, 20 and 40 respectively, with initial condition: (x_0 = –2.0, p_0 = 0.0).





Phase portraits for the classical and quantum Henon-Heiles oscillators subjected to an external electric field of strength g and frequency ω; case A: ω = 0.3, 0.7; g = 0.0, 0.5, 1.0; case B: ω = 0.7, g = 0.0, 0.5, 1.0;ω = 0.3, g = 0.0, 0.5, 0.8.

$$H(x,y) = \frac{1}{2}\left(p_x^2 + p_y^2\right) + \frac{1}{2}\left(x^2 + y^2\right) + \lambda\, x\left(y^2 - \frac{x^2}{3}\right) - g\, y \cos\,(\omega t)$$

$$\lambda = 0.1118034$$

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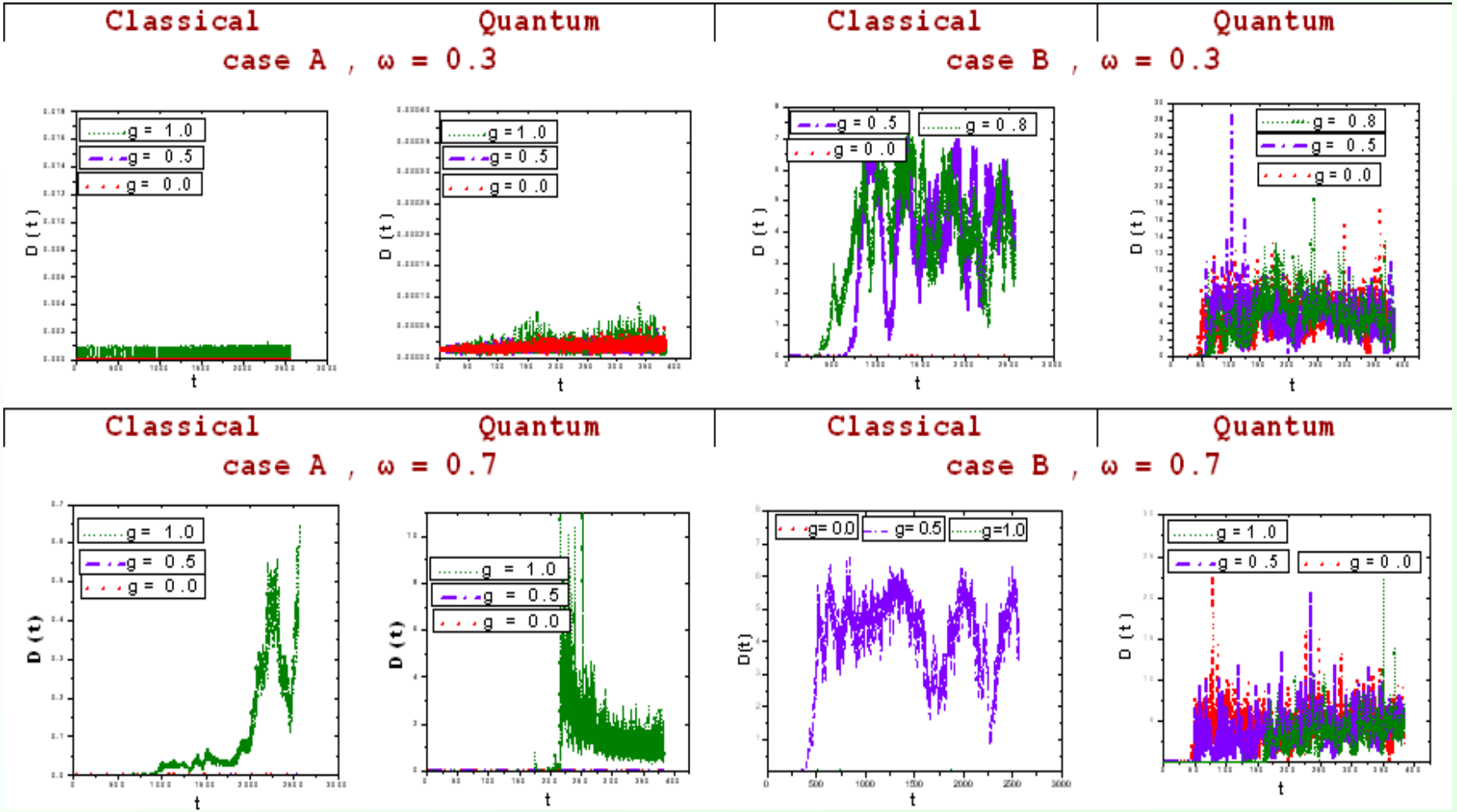

Phase space distance function D(t) for the classical and quantum Henon-Heiles oscillators in the presence of an external electric field of strength g and frequency ω; case A: ω = 0.3, 0.7; g = 0.0, 0.5, 1.0; case B: ω = 0.7, g = 0.0, 0.5, 1.0;ω = 0.3, g = 0.0, 0.5, 0.8.

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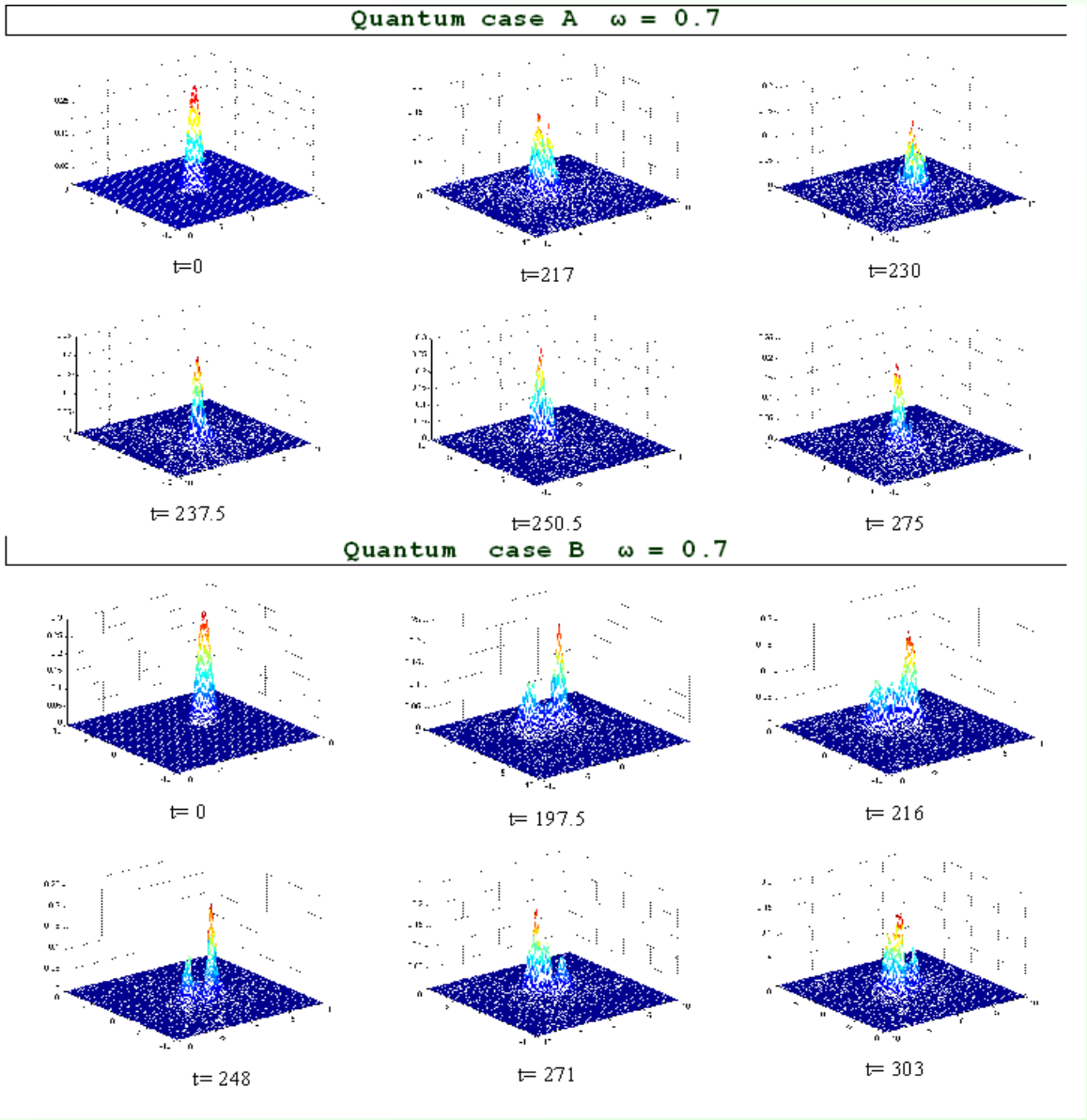
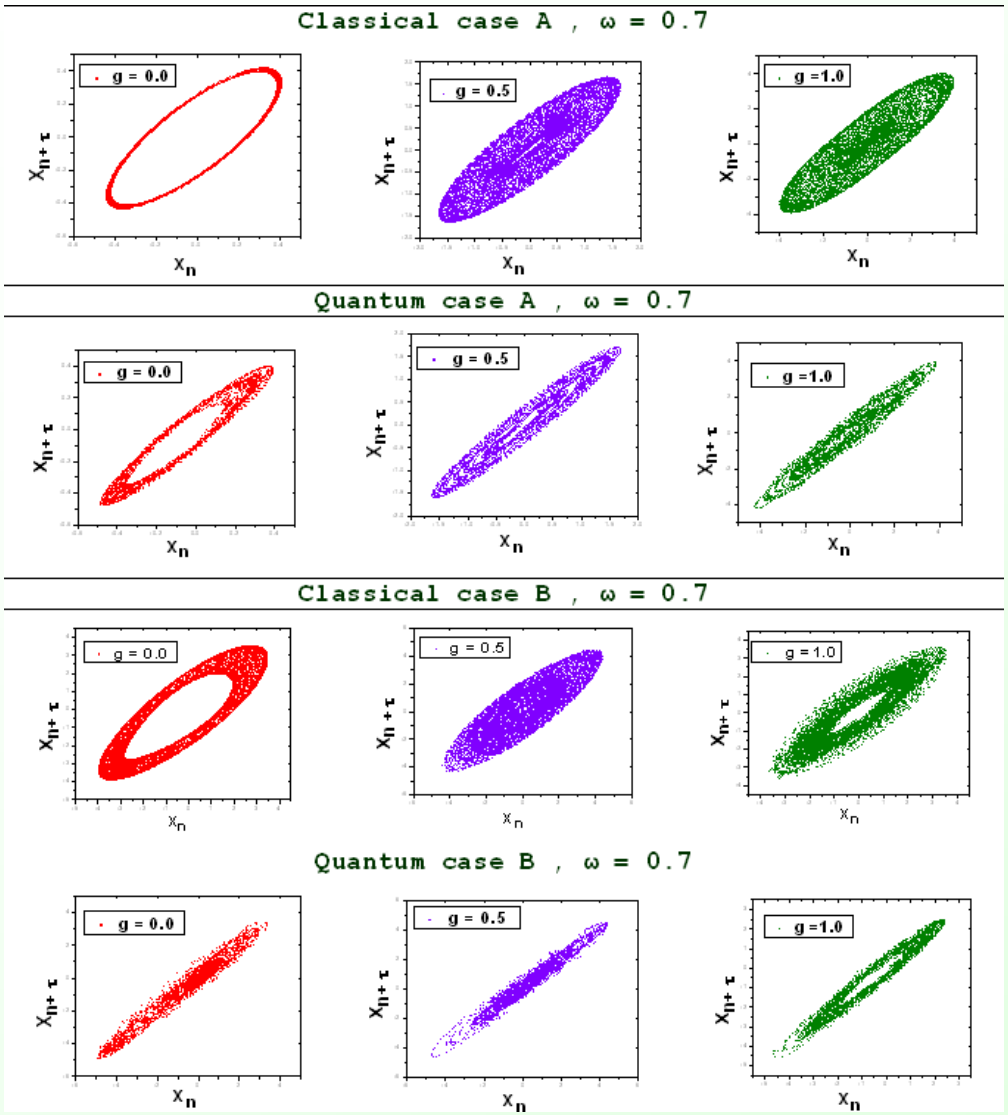


Probability density plots at different time steps for the quantum Henon - Heiles oscillator subjected to an external electric field of strength g = 1.0 and the frequency ω = 0.7 for both cases A and B.



Return maps of the position coordinate x for the classical and quantum Henon - Heiles oscillators subjected to an external electric field of strength g = 0.0, 0.5, 1.0 and the frequency ω = 0.7

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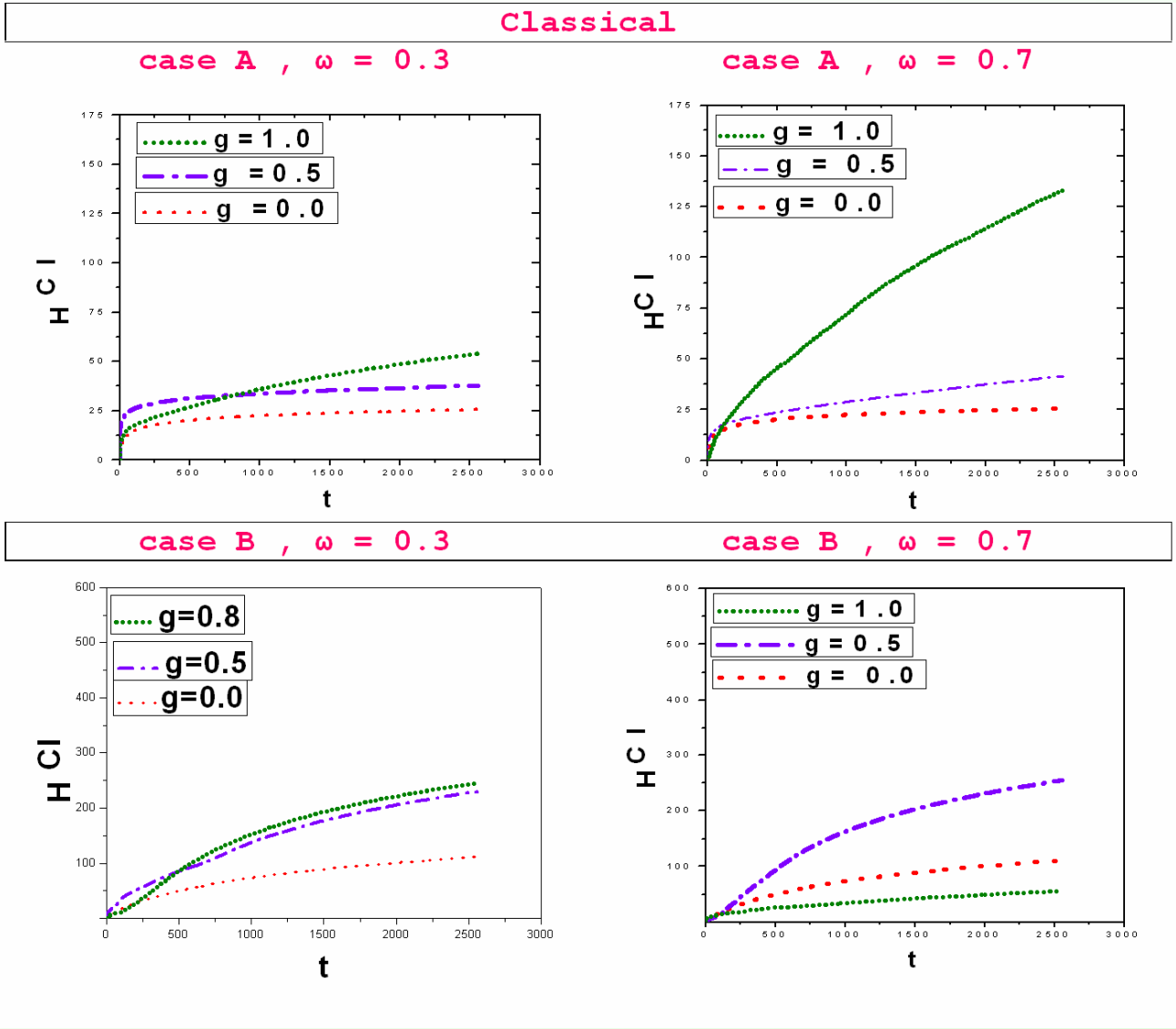
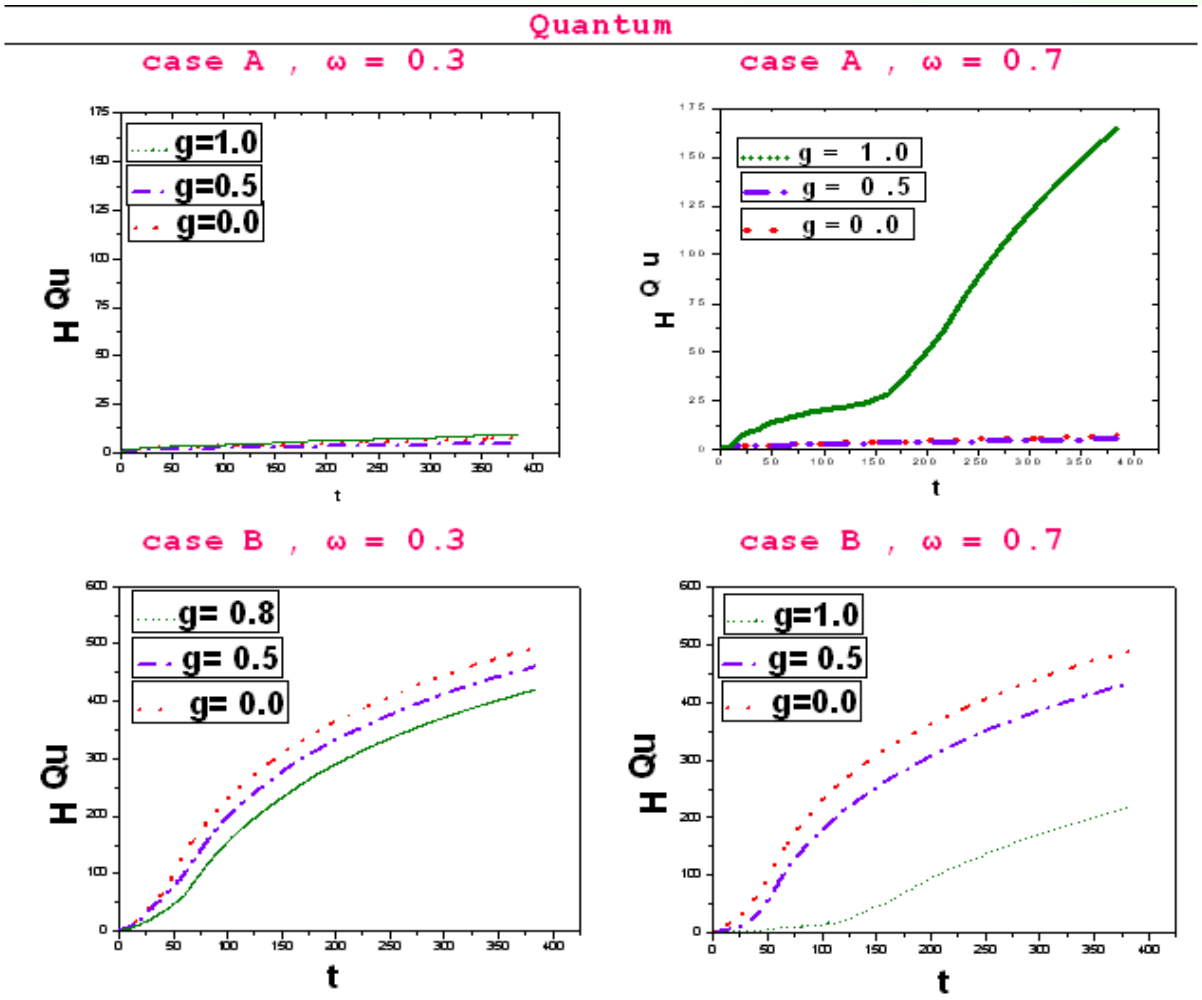


Time evolution of the KSL entropy for the classical Henon-Heiles oscillator in the presence of an external electric field of strength g and frequency ω; case A: ω = 0.3, 0.7; g = 0.0, 0.5, 1.0; case B: ω = 0.7, g = 0.0, 0.5, 1.0;ω = 0.3, g = 0.0, 0.5, 0.8.



Time evolution of the KSL entropy for the quantum Henon - Heiles oscillator in the presence of an external electric field of strength g and frequency ω; case A: ω = 0.3, 0.7; g = 0.0, 0.5, 1.0; case B: ω = 0.7, g = 0.0, 0.5, 1.0;ω = 0.3, g = 0.0, 0.5, 0.8.

P. K. Chattaraj, S. Sengupta and S. Giri , J. Chem. Sci., 120, 33 (2008)

"Rydberg atoms and molecules – Testing grounds for quantum manifestations of chaos"

Ref: M. Lakshmanan and K. Ganesan, *Curr. Sci. 68* (1995) 38.

"In recent times it has been found that highly excited Rydberg atoms and molecules (which are effectively one – electron systems) under various external fields are veritable gold mines for exploring the quantum aspects of chaos. These systems are particularly appealing as they are not merely mathematical models but important physical systems which can be realized in the laboratory. Particular examples are the hydrogen atom in external magnetic fields, crossed electric and magnetic fields, van der Waals force, periodic micro-wave radiation and so on."

"Hydrogen atom in an external oscillating electric field ($H' = Fz \cos\omega t$) exhibits order to chaos transition depending on F and ω values" : Ref: G. Casati, B. V. Chirikov, I. Guarneri and D. L. Shepelyansky, Phys. Rep. 154 (1987) 77.

"…. One requirs an astronomical field strength in order to realize the effect of chaos in H- atom in ground state … for highly excited Rydberg atoms (say $n \approx 50$) there is a dramatic reduction of the field strength (of the order of Coulomb field is enough) required to realize the effect of chaos . .".

Ref : M. Lakshmanan and K. Ganesan, *Curr. Sci.* 71 (1996) 134.
P. K. Chattaraj and S. Sengupta, Curr. Sci. 71 (1996) 134.

Numerical Solution :

TDSE (in a.u.) : $[-\frac{1}{2}\nabla^2 \underbrace{-\frac{1}{r}+F\,z\,\cos\omega t}_{V})\Psi = i\frac{\partial\Psi}{\partial t}$ (1)

i) Cylindrical polar coordinate system ($\tilde{\rho}, z, \Phi$) : $r = \sqrt{\tilde{\rho}^2 + z^2}$

ii) $y = \tilde{\rho}\,\Psi$

ii) $\tilde{\rho} = x^2$

iv) Integration over $0 \le \Phi \le 2\pi$ has been done analytically.

$$\Downarrow$$

$$\left[\frac{3}{4x^3}\frac{\partial y}{\partial x} - \frac{1}{4x^2}\frac{\partial^2 y}{\partial x^2} - \frac{\partial^2 y}{\partial z^2}\right] - \left[\frac{1}{x^4} - 2V\right] y = 2i\frac{\partial y}{\partial t} \qquad (2)$$

Eqn. (7) is solved as an initial boundary value problem using an alternating direction implicit (ADI) method. Resulting tridiagonal matrix eqn. is solved using Thomas algorithm. Each ADI cycle corresponds to $2\Delta t$.

Boundary conditions :

At t=0 , y (x, z) is known for $\forall\ x, z$

y (0, z) = 0 = y(∞, z) $\forall$ z, t

y (x, ±∞) = 0 $\forall$ x, t

$\Delta x = \Delta z = 0.4$; $\Delta t = 0.01$; $\omega = 5\pi$ (stability)

At t = 0 Ψ_{1s} and Ψ_{20s}

F = 0 and F = 5

a) Numerical scheme is stable due to the presence of 'i'.

Ref. P. K. Chattaraj, K. S. Rao and B. M. Deb, *J. Comp. Phys.* 72 (1987) 504.

b) Total energy values remain conserved in zero field cases.

c) Ψ is moved forward by 500 time steps and then taken back to its initial position where the original profile is reproduced in all cases within the prescribed tolerance limit.

Quantum Theory of Motion for a Many – Particle System

(P. R. Holland, 1993)

Wave function in 3N-D Configuration space

N point particle in 3-D Euclidean space

QFDFT

$\Phi(\vec{r},t)$ is in 3- D Euclidean space

Both "wave and particle" in Euclidean space

GNLSE $[-\frac{1}{2}\nabla^2 + v_{eff}(\vec{r},t)]\Phi(\vec{r},t) = i\frac{\partial\Phi(\vec{r},t)}{\partial t}$; $\rho(\vec{r},t) = |\Phi|^2$; $\vec{j}(\vec{r},t) = [\Phi_{re}\Phi_{im} - \Phi_{im}\Phi_{re}]$

Test Case :

Bohmian trajectory of He atom (^{1}P state) interacting with an external electric field.

Velocity Eqn. ⇒ 2nd – order Runge – Kutta Method

At t = 0, $\tilde{\rho} = 0.104976$ au , z = 0.108000 au

Chaotic Ionization of Highly Excited He - atoms

Ref : **Exptl :**

D. R. Mariani et al , *Phys. Rev. Lett.* 50 , 1261 (1983) ;
—— , *Phys. Rev. A* 42 , 573 (1990).

Theoretical:

M. M. Sanders and R. V. Jensen , *Am. J. Phys.* 64 , 1013 (1996).

Chaotic Ionization of Rydberg He atoms

$$H(\vec{r},\vec{p},t) = \frac{\vec{p}.\vec{p}}{2} + v_{core}(\vec{r}) + v_{ext}(\vec{r},t)$$

$$v_{core}(\vec{r}) = v_n(\vec{r}) + v_s(\vec{r}) + v_p(\vec{r})$$

$v_n(\vec{r}) = -\frac{2}{r}$ [coulomb int. bet the Rydberg e$^-$ and the unshielded He nucleus]

$v_s(\vec{r}) = \frac{1}{r}(1-(1+2r)e^{-4r})$ [Shielding pot. $\Rightarrow$ Work reqd. to move a pt. outer electron from $\propto$ to r thro´ the charge cloud associated with unperturbed inner 1s e$^-$ - orbital.]

$$v_p(\vec{r}) = -\frac{9}{64r^4}(1-(1+4r+24r^2+\frac{160}{3}r^3+\frac{64}{3}r^4)\frac{e^{-4r}}{3}-\frac{2}{3}(1+2r)^4e^{-8r})$$

[Core polarization $\Rightarrow$ Correction to $v_s(\vec{r})$ stemming from the distortion of 1s wf of the core e$^-$ by the Rydberg e$^-$ (Bethe, 1933)]

$$v_{ext}(\vec{r},t) = 0.5\,z\,\varepsilon'[\sin(\omega_0 t)+\sin(\omega_1 t)]$$

$$\Psi(\vec{r}, t=0)$$

$$R_{1\,0}(\vec{r}) = 2z^{3/2}\exp[-zr] \quad \Big| \quad \rho = \frac{2z}{n}r$$

$$R_{n\,0}(\vec{r}) = -\left\{\left(\frac{2z}{n}\right)^3 \frac{(n-1)!}{2n(n!)^3}\right\}^{\frac{1}{2}} e^{-\frac{\rho}{2}} L_n'(\rho)$$

$$L_n'(\rho) = \sum_{k=0}^{n-1}(-1)^{k+1}\frac{(n!)^2}{(n-k-1)!(k+1)!k!}\rho^k$$

$1s^2$ & $1s15s$ $\Rightarrow$ 1 - normalized

ES $\Rightarrow$ TDSE with $H(\vec{r},\vec{p},t)$ as above $\Psi(\vec{r},t=0) = R_{15\,0}(r)\ \gamma_{00}(\theta,\phi)$

GS $\Rightarrow$ GNLSE $\Psi(\vec{r},t=0) = \Psi_{HF}^{He}$ (1 – normalized)

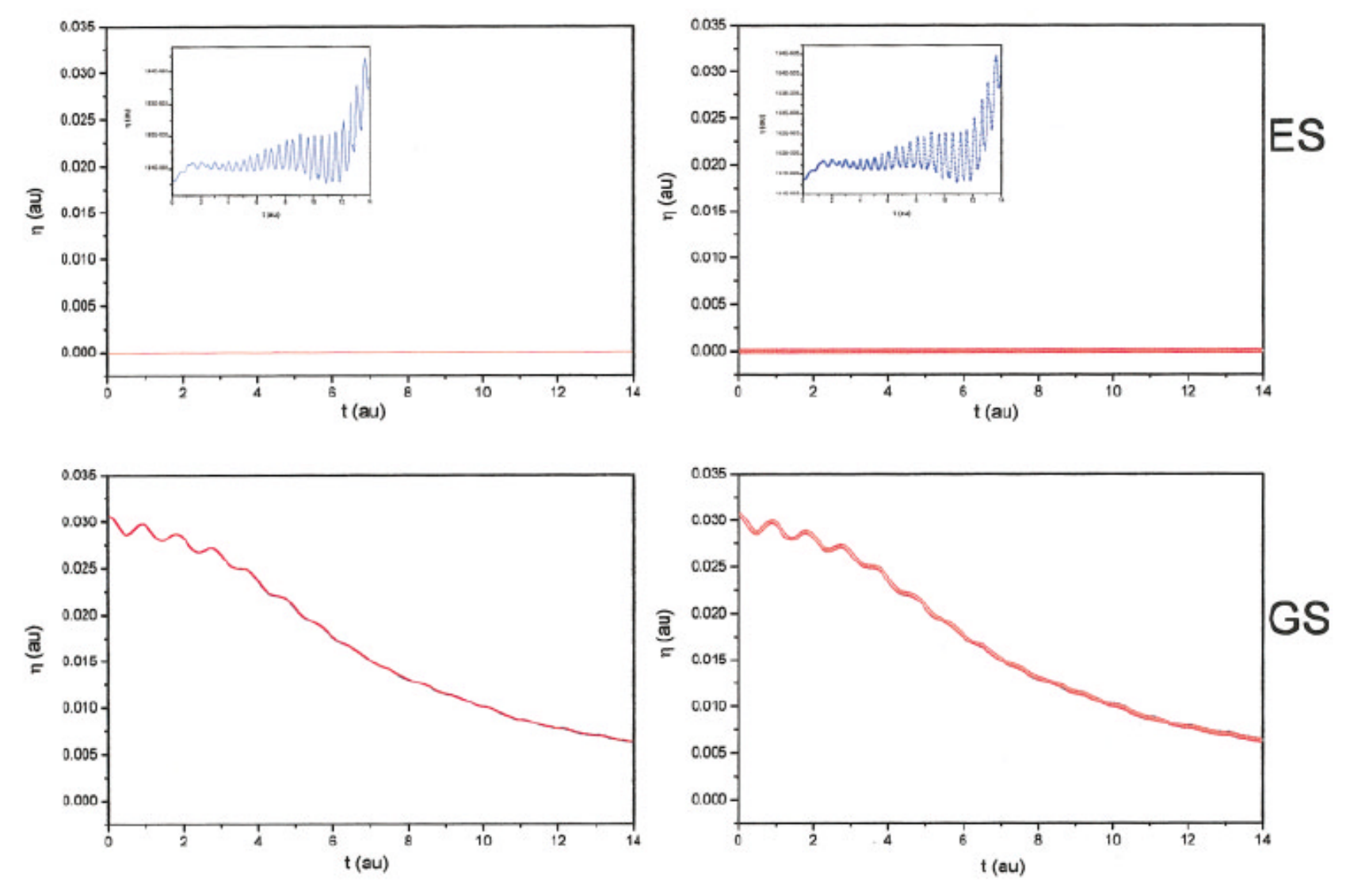


FIGURE 4. Time evolution of chemical hardness (η, a.u.) when a hydrogen atom is subjected to external electric fields.

P. K. CHATTARAJ & U. SARKAR, *INT. J. QUANTUM CHEM.* 91 (2003) 633

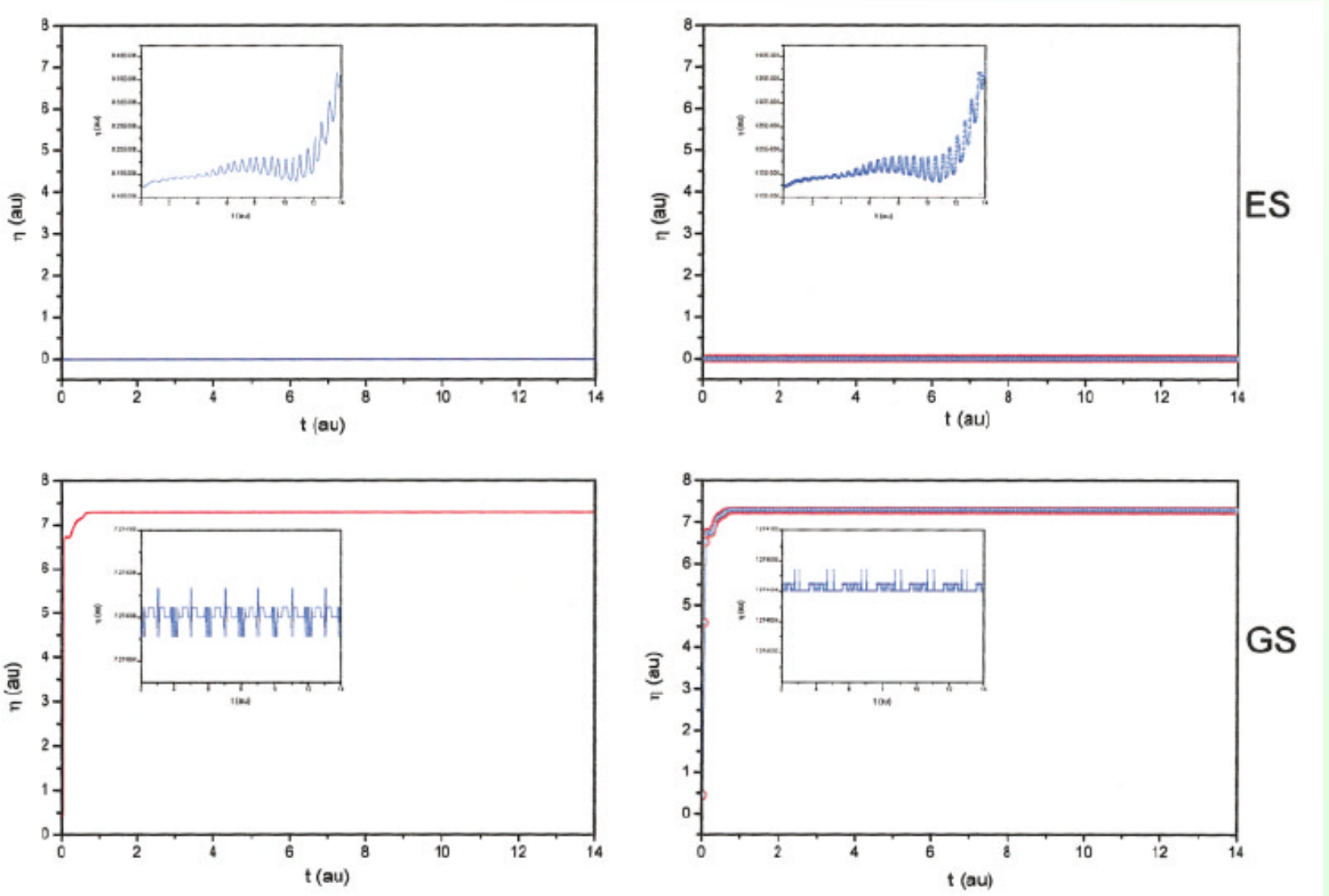


FIGURE 5. Time evolution of chemical hardness (η, a.u.) when a helium atom is subjected to external electric fields.

P. K. CHATTARAJ & U. SARKAR, *INT. J. QUANTUM CHEM.* 91 (2003) 633

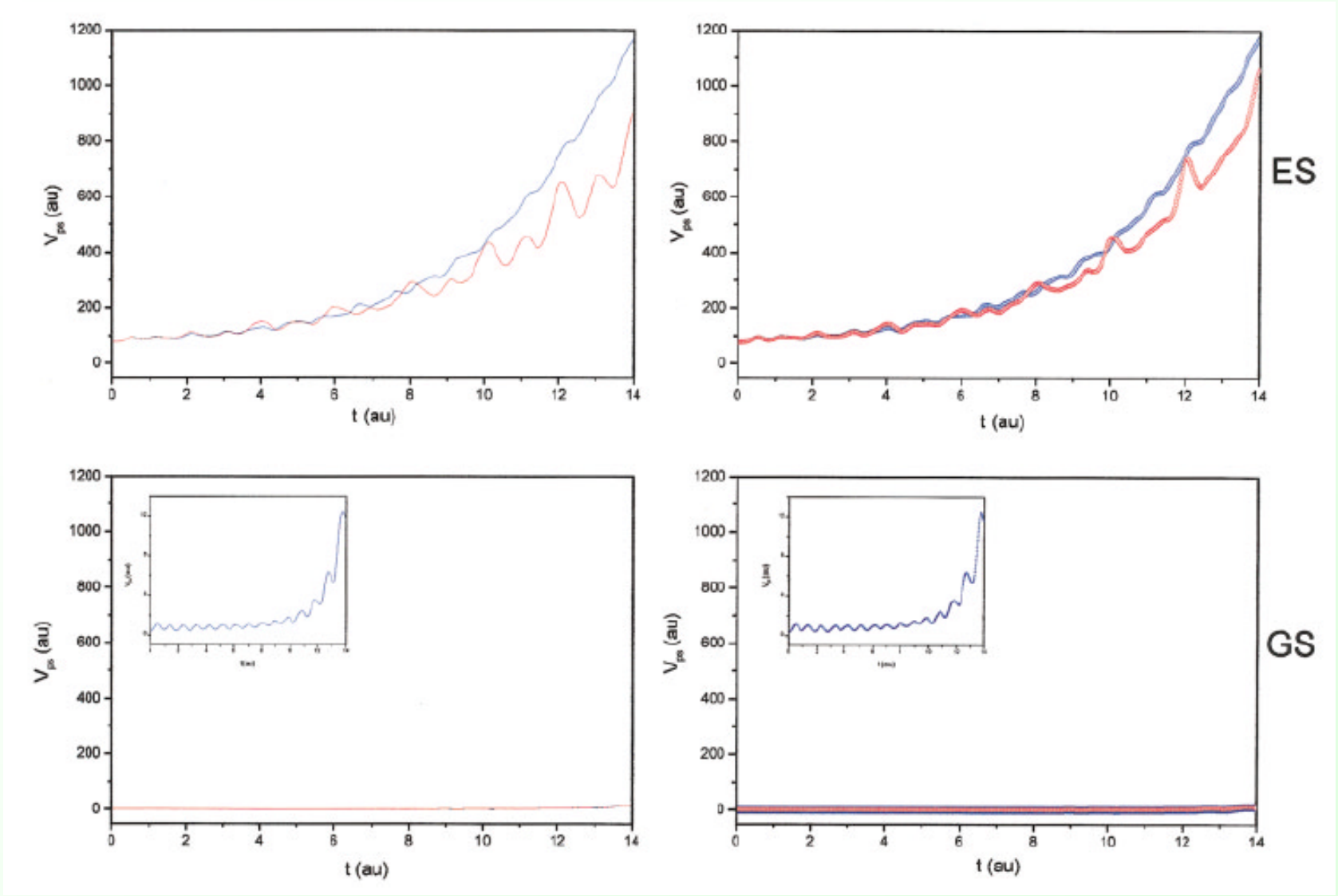


FIGURE 10. Time evolution of phase volume (V_{ps}, a.u.) when a hydrogen atom is subjected to external electric fields.

P. K. CHATTARAJ & U. SARKAR, *INT. J. QUANTUM CHEM.* 91 (2003) 633

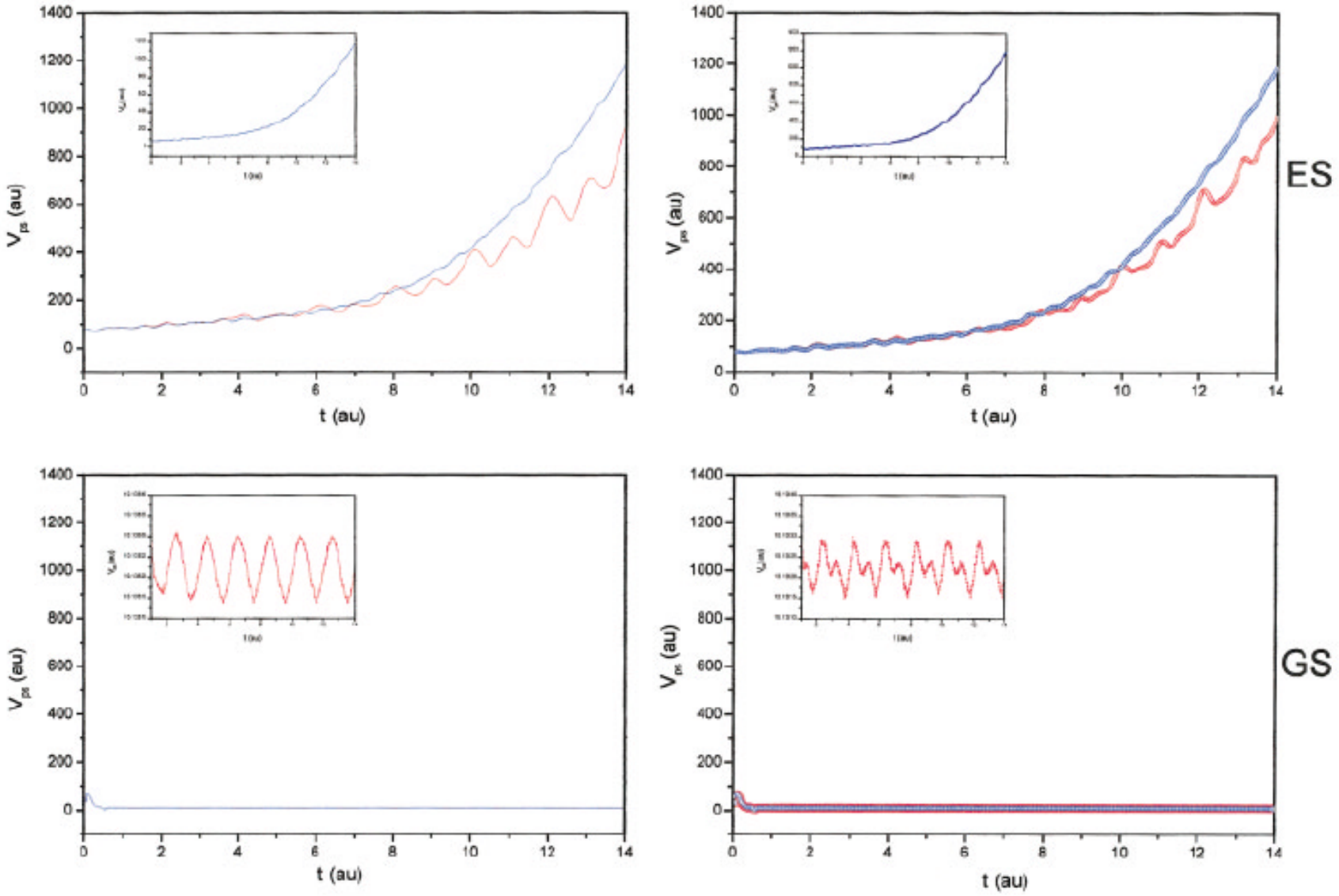


FIGURE 11. Time evolution of phase volume (V_{ps}, a.u.) when a helium atom is subjected to external electric fields.

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Thank You