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Semi-classical versus exact eigenvalues of He–benzene using cross-correlation filter-diagonalization

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Abstract

We determine semi-classically the eigenvalues of a He–benzene model where the benzene is held fixed in space (and non-rotating). The results are analyzed with an efficient approach toward extracting the eigenvalues from a short-time (set) of correlation functions: cross-correlation filter-diagonalization. The use of this analysis tool allows quite accurate determination of the eigenvalues, when compared to exact eigenvalues. One of the reasons that the eigenvalues are so accurate is that the cross-correlation filter-diagonalization approach allows the use of very short times, for which semi-classical is very accurate. © 2000 Elsevier Science B.V.

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1. Introduction

The problem of extracting excited vibrational states for floppy van der Waals (vdW) systems is fundamental for our understanding of cluster dynamics and of potential-surfaces. Existing approaches for extracting rovibrational information for clusters include exact grid based methods [1–8]; vibrational configuration-interaction and mean-field methods and their hybrids [9–11]; and variational Monte-Carlo methods [12–14]. For large systems it is desirable to have, however, complementary methods which scale gently with system size and are accurate. In this work, we focus on the use of semi-classical dynamics [15–22] for a non-trivial system at low excitations, where the overall phase-space sampled is not too large, so that convergence of the technique could be achieved using both semi-classical and standard exact techniques, allowing comparison.

There are two issues relevant to semi-classical techniques: how accurate these techniques are, and how much numerical effort (trajectories) is required. Typically the numerical effort in semi-classical methods increases with propagation (signal) time. Therefore, a simple approach to reduce the effort is to apply methods that extract the numerical effort from a short-time sample of the correlation function. One such method is filter-diagonalization [4,5,23–30].

Filter-diagonalization has been applied to many systems, including semi-classical systems. The original applications to semi-classical extraction of eigenvalues were done with the original single-correlation function formalism (see e.g. Refs. [24,31]). In this work, we present the application of a very efficient (as far as signal time-length) modification, cross-correlation filter-diagonalization. This approach, introduced several years ago [26], has been previously applied to extract resonance

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and bound eigenvalues from a signal generated exactly [25] and from a semi-classically generated correlation function for a tunneling splitting [28]. In this work, we study its performance systematically for a challenging vdW system, He–benzene (for rigid infinitely heavy benzene), and verify the surprising overall accuracy of the results.

The plan of the letter is as follows. In Section 2 we briefly review the methodology. Section 3 shows the results and Section 4 concludes with future outlooks.

2. Methodology

There are two separate parts to the simulation: the generation of a cross-correlation function semi-classically, and the analysis of this cross-correlation to extract bound-state eigenvalues.

2.1. Semi-classical dynamics

The starting time-dependent cross-correlation function is ($\hbar = 1$)

$$D_{ii'}(t) = \langle \Phi_i | \exp(-\mathrm{i}Ht) | \Phi_{i'} \rangle, \tag{2.1}$$

where $i, i' = 1, \ldots, I_{\text{primitive}}$, and $I_{\text{primitive}}$ is the number of cross-correlation 'primitive' (meaning purely Gaussian) functions. In this work we use up to $I_{\text{primitive}} = 30$ Gaussian basis-functions, and then symmetrize the cross-correlation functions as explained below. The cross-correlation function is calculated with a standard semi-classical algorithm, the Herman–Kluk approach [15,17,18],

$$\begin{aligned} D_{ii'}(t) = \int\!\!\int & \mathrm{d}q_0\, \mathrm{d}p_0 \langle \Phi_i | g_{q_f(t) p_f(t)} \rangle F \\ & \times (q(t), p(t), q_0, p_0) \\ & \times \exp(\mathrm{i}S) \langle g_{q_0 p_0} | \Phi_{i'} \rangle, \end{aligned} \tag{2.2}$$

where one chooses by a Monte-Carlo algorithm the initial momentum and average position of the starting Gaussian ($g_{q_0 p_0}$) for the evaluation of the wavefunction, and the classical trajectory $(q(t), p(t))$ is defined by its initial position and momentum. S is the action associated with the trajectory, and F is a method-dependent amplitude function. In our calculation we made a simple modification to the usual form of F to account for the fact that the frequencies associated with in-plane and out-of-plane motions are very different for the He–benzene IPS employed (the frequencies determined from the force-constant matrix at the minimum potential point are $\omega_x = \omega_y = 19.351\ \mathrm{cm}^{-1}$ vs. $\omega_z = 60.125\ \mathrm{cm}^{-1}$ for in-plane and out-of-plane motions, respectively). This implies that in the development of the Herman–Kluk semi-classical formalism, ellipsoidal (non-isotropic) Gaussians should be used for optimal performance, with different widths associated with different axes. The final formula can be straightforwardly shown to be simply:

$$\begin{aligned} F = & \sqrt{\det\left(\frac{\partial \bar{q}(t)}{\partial \bar{q}_0} + \frac{\partial \bar{p}(t)}{\partial \bar{p}_0} + \mathrm{i}\frac{\partial \bar{p}(t)}{\partial \bar{q}_0} - \mathrm{i}\frac{\partial \bar{q}(t)}{\partial \bar{p}_0} \right)} \\ & \times \left(\frac{1}{2\pi} \right)^{N_\mathrm{d}}, \end{aligned} \tag{2.3}$$

where N_d is the number of dimensions and we introduce the scaled coordinates,

$$\begin{aligned} \bar{q}_a(t) &= \frac{q_a(t)}{\sigma_a}, \\ \bar{p}_a(t) &= \sigma_a p_a(t), \end{aligned} \tag{2.4}$$

and the widths are simply

$$\sigma_a = \frac{1}{\sqrt{M\omega_a}}, \quad a = x, y, z \tag{2.5}$$

where M is the helium mass.

2.2. Symmetrization

The next stage is the proper symmetrization of the correlation function, since the molecule has symmetry (here C_{6h}, although we do not take into account the inversion symmetry since the splittings it introduced are too small). This is done as follows. Each of the initial primitive functions Φ_i is taken to be a Gaussian concentrated at an initial 3-D position $\vec{r}_i$. (The momentum of these initial Gaussians is taken as zero more general choices would be pursued in the future.) We place the Gaussians in rings, each containing six Gaussians, which are related by a C_6 operation, and relabel the overall basis-function index i as j, k. The functions are now written as Φ_{jk}, where $k = 1, \ldots, 6$ is the index of the function within the ring and $j = 1, \ldots, J$ is the ring index (where J is the number of rings). We then formally write the properly symmetrized combinations for any symmetry (the symmetry label is assumed implicitly but not denoted in the formulae below) as

$$\Psi_{jn} = \sum_k T_{kn}\Phi_{jk}, \tag{2.6}$$

where n is either 1 (for a one-dimensional representation) or 1, 2 (for a two-dimensional representation). The final correlation function is then

$$C_{jn,j'n'}(t) = \sum_{k,k'} U_{kn,k'n'} D_{jk,j'k'}, \tag{2.7}$$

where from the previous discussion it is clear that the simplest choice for the coefficient matrix is $U_{kn,k'n'} = T_{kn}T_{k'n'}$. However, better statistics is obtained if we use the symmetry property of the correlation function,

$$D_{jk,j'k'} = D_{j\mathrm{mod}(k+m,6),j'\mathrm{mod}(k'+m,6)}, \tag{2.8}$$

where $m = 0, \ldots, 5$. This leads to the final expression

$$U_{kn,k'n'} = \sum_m T_{\mathrm{mod}(k+m,6)n} T_{\mathrm{mod}(k'+m',6)n'}. \tag{2.9}$$

2.3. Signal extraction – filter diagonalization

Once $C(t)$ is available, the next step is seemingly trivial: Fourier-transform $C(t)$ and then extract the vibrational frequencies from the peaks. As mentioned, however, a difficulty in any semi-classical calculation is that it tends to numerically break down at long times as the phases from different trajectories interfere destructively. To reduce this problem, increasingly sophisticated amplitude functions (F) have been invented. Nevertheless, at some point in time these start increasing in magnitude and thus also tend to destroy the numerical convergence of $C(t)$.

To avoid these problems we use here filter-diagonalization, an approach toward extracting frequencies from either a quantum correlation function or a general signal. The method has been presented in many publications so we only present its most relevant points. In this method we first choose a set of a few (L) energies in the spectral region of interest, E_l, $l = 1, \ldots, L$, and Fourier-transform each initial wavefunction $|\Psi_{jn}(t)\rangle$ for a *short* time T at each of these energies,

$$\psi_{jn,l} = \sum_t \exp(\mathrm{i}E_l t)\Psi_{jn}(t), \tag{2.10}$$

where we used the elegant discrete-transform approach of Ref. [27] rather than the original continuous-transform approach [26]. (The size of this $|\psi_{jn,l}\rangle$ set is $M \equiv JL$ or $M \equiv 2JL$, i.e., the number of rings times the number of sampled energies, times 2 for a 2-D irreducible representation.) The resulting functions are approximate eigenstates of H. More precisely, each of these functions contains essentially only contributions from the spectral range of interest. If the total number of these functions, M, is sufficiently large, the $|\psi_{jn,l}\rangle$ will thus become a basis which *spans the eigenstates* in the spectral range of interest. Therefore, the eigenvalues of H in the spectral range of interest, labeled ε, can be extracted by diagonalizing H in this (non-orthogonal) energy-selective basis through the solution of the (small) $M \times M$ equation:

$$uB = SB\varepsilon, \tag{2.11}$$

where, in the notation used above,

$$\begin{aligned} u_{jnl,j'n'l'} &= \left\langle \psi_{jnl} \middle| \exp(-\mathrm{i}H\,\mathrm{d}t) \middle| \psi_{j'n'l'} \right\rangle \\ s_{jnl,j'n'l'} &= \left\langle \psi_{jnl} \middle| \psi_{j'n'l'} \right\rangle, \end{aligned} \tag{2.12}$$

where B is the eigenvector coefficient matrix. A key realization was that the u, s matrices can be written directly in terms of the correlation function, $C(t)$, and, further, the formulae are quite elegant if one uses a discrete Fourier transform, e.g.,

$$s_{jnl,j'n'l'} = \sum_{tt'} \exp(-\mathrm{i}E_l t + \mathrm{i}E_{l'} t')C_{jn,j'n'}(t - t'). \tag{2.13}$$

The final formulae are natural extensions of the Fourier method, and enjoy its power while requiring shorter signal lengths.

While even the single correlation function (a single j, n) version of filter-diagonalization requires less signal time than a Fourier-transform – as do other methods, such as MUSIC, linear-prediction, maximum-entropy, etc. (for a review see Ref. [32]) – the use of a cross-correlation function makes filter-diagonalization quite powerful, as shown below, as it facilitates the separation of even closely spaced eigenvalues at short times.

3. Results

To examine the use of cross-correlation functions, we studied a sample vdW problem, the eigenvalues of the three-dimensional He–benzene system (with the benzene held fixed). This problem is amenable to exact investigation, while also being a challenge for semi-classical methods owing to the large anharmonicities in the potential surface (the ground to first excited-state level spacing, 11.1 wavenumbers, is smaller by a factor of almost two than the smallest in-plane frequency as obtained from the force-constant matrix).

The Hamiltonian used here has a simple three-dimensional vdW pair-potential for the He, interacting with each of the atoms in benzene [33]:

$$H = \frac{\mathbf{p}^2}{2M} + \sum_{i=1}^{6} v_{\mathrm{HeC}}(\mathbf{r} - \mathbf{r}_{C_i}) + \sum_{i=1}^{6} v_{\mathrm{HeH}}(\mathbf{r} - \mathbf{r}_{H_i}), \tag{3.1}$$

with

$$v_{\mathrm{HeC}}(\mathbf{r}) = 4\varepsilon_{\mathrm{HeC}}\left[\left(\frac{\sigma_{\mathrm{HeC}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{HeC}}}{r}\right)^{6}\right], \tag{3.2}$$

and v_{HeH} similarly defined. The parameters for the Lennard–Jones functions are recorded in Table 1.

The exact simulations were done using standard grid techniques: a single random-valued wavepacket was propagated in time [34] and the correlation function was analyzed by filter-diagonalization [4,26,27]. We checked convergence with grid parameters.

Turning to the semi-classical simulations, Fig. 1 shows schematically the location of some of the initial Gaussians. Table 2 records the values of the initial location of the Gaussian functions and other parameters used in the simulations. Up to five rings were used; for most symmetries, all rings can participate, but for the B_1 symmetry only rings with Gaussians that are at the same angles as the carbons can be used (rings 1–3) while for the B_2 symmetry only the staggered rings (4–5) can be used. Since $L = 2$–7 sampled energies were used,

Table 1
Parameters used in the simulations (see also Table 2 for Gaussian placement)[a]

Time-step (dt)	10.618 fs (= 0.002/cm^{-1})
He mass (M)	0.12 (cm^{-1}Å^2)$^{-1}$
σ_{HeC}	3.099 Å
$\varepsilon_{\mathrm{HeC}}$	13.92 cm^{-1}
σ_{HeH}	2.903 Å
$\varepsilon_{\mathrm{HeH}}$	5.761 cm^{-1}
Minimum potential	−100.317 cm^{-1}
Location of minimum potential	(0, 0, 3.148) Å
Position of first C (in benzene)	(1.40, 0, 0) Å
Position of first H (in benzene)	(2.48, 0, 0) Å
Number of sampled energies (L)	2–7

[a] Note that cm^{-1} refers here to an energy unit, wavenumbers.

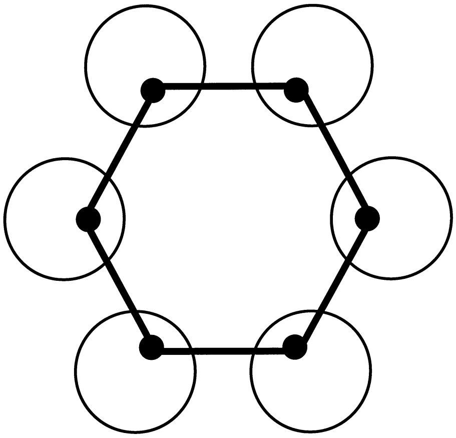

Fig. 1. Planar schematics of the position of each initial Gaussian in one ring, relative to the benzene atoms. Note that the plane of the initial Gaussian wavepackets is set above the benzene plane by $z = 3.148$ Å.

Table 2
Locations of the initial Gaussians[a]

(2.75, 0, 3.148) Å
(1.75, 0, 3.148) Å
(0.75, 0, 3.148) Å
(2.38, 1.375, 3.148) Å
(1.52, 0.875, 3.148) Å

[a] Each entry is the first member of a ring of six Gaussians, related one to each other by a C_6 symmetry. Rings 1–3 were aligned with the C–H angular positions, and rings 4–5 were staggered (see also Fig. 1).

the size (M) of the matrices in Eq. (3.3) was, for all eigenvalues except those of the B representation, up to $2JL = 2 \times 5 \times (2–7)$.

The semi-classical calculation, Eq. (3.4), necessitates the propagation of classical trajectories. We used a fourth-order Runge–Kutta fixed time-step algorithm.

Fig. 2 shows the dependence of the results on the number of cross-correlation functions for a single probed eigenvalue (the first excited state of the one-dimensional irreducible representation, A_1) and a small number of trajectories (500). Results are compared for a calculation using one ring and with five rings (i.e., for a 1×1 and a 5×5 time-dependent symmetrized correlation function). The use of multiple correlation functions, even for a small number of trajectories, reduces the total time necessary.

Table 3 shows the converged results from a larger number of trajectories (500–10 000) in comparison to the exact values. The values are quite accurate. This is both a result of the intrinsic properties of semi-classical propagation, and also a result of the short time used (since the Herman–Kluk approach, like other semi-classical methods, is exact at short times).

Overall, the results are quite accurate, within about half a wavenumber. There are several parameters in the calculation, most notably the total signal-length used. However, in practice it is easy to choose this and other parameters by stability of the results. In addition, we find that another parameter, the imaginary part of each eigenvalue (which vanishes rigorously and exists only due to numerical imprecision in calculating the correlation function by a Monte-Carlo algorithm) tends to vanish at precisely the times when the real part of the eigenvalue is most stable. These two criteria lead to precise determination of the eigenvalues.

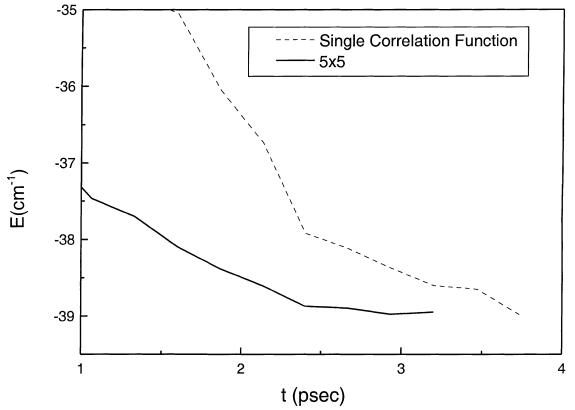

Fig. 2. Convergence with time of eigenvalues for the first excited state of the A_1 symmetry, for a 5×5 (solid) vs a 1×1 (dashed) fully symmetrized correlation function.

Table 3
Converged results from a 5×5 cross-correlation analysis vs exact results for different symmetries[a]

Symmetry	Semi-classical	Exact
A_1	−56.5	−56.57
E_1	−46.0	−45.46
A_1	−38.8	−38.77
E_2	−37.7	−36.96
E_1	−32.6	−32.45
B_2	−31.4	−30.92
B_1	−30.2	−29.39
A_1	−28.0	−27.82
E_2	−27.2	−26.99

[a] All energies are in wavenumbers.

4. Discussion

The high quality of the results examined here and in previous studies show that floppy vdW systems can be examined with semi-classical methods. As shown here, the results are quite accurate when the signal is both symmetrized and used with a cross-correlation filter-diagonalization algorithm.

In this study, the number of degrees of freedom was limited to a small number (three), so that the results could be compared to grid studies. Future applications of cross-correlation filter-diagonalization to this problem would examine the dependence of the eigenvalues on the benzene vibrational degrees of freedom, and on vibrational excitation. The next, and non-trivial step, would be the incorporation of the rotational motion.

There are several other methodological advances which can be envisioned. One would be the use of interaction picture techniques [16] for improving the convergence of the correlation function. This would be useful for studies involving clusters of weakly interacting He particles. Another would be the use of an improved filter-diagonalization equation, where the propagator matrix u is replaced by a Hamiltonian matrix h evaluated by Monte-Carlo methods [30,35].

Overall, the study shows that with the proper cross-correlation filter-diagonalization analysis tool, semi-classical calculations are very powerful for studying floppy vdW systems.

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References

[1] A. Bahel, Z. Bacic, J. Chem. Phys. 111 (1999) 11164–11176.

[2] R.S. Fellers, C. Leforestier, L.B. Braly, M.G. Brown, R.J. Saykally, Science 284 (1999) 945–948.

[3] J.M. Hutson, S.Y. Liu, J.W. Moskowitz, Z. Bacic, J. Chem. Phys. 111 (1999) 8378–8383.

[4] W. Kim, D. Neuhauser, M.R. Wall, P.M. Felker, J. Chem. Phys. 110 (1999) 8461–8475.

[5] V.A. Mandelshtam, T.P. Grozdanov, H.S. Taylor, J. Chem. Phys. 103 (1995) 10074–10084.

[6] H. Chen, S. Liu, J.C. Light, J. Chem. Phys. 110 (1999) 168–176.

[7] B. Fehrensen, D. Luckhaus, M. Quack, Chem. Phys. Lett. 300 (1999) 312–320.

[8] O.L. Polyansky, R. Prosmiti, W. Klopper, J. Tennyson, Mol. Phys. 98 (2000) 261–273.

[9] S.K. Gregurick, J.H.Y. Liu, D.A. Brant, R.B. Gerber, J. Phys. Chem. B 103 (1999) 3476–3488.

[10] S. Carter, J.M. Bowman, J. Phys. Chem. a 104 (2000) 2355–2361.

[11] K. Drukker, S. Hammes Schiffer, J. Chem. Phys. 107 (1997) 363–374.

[12] B. Bernu, D.M. Ceperley, W.A. Lester, J. Chem. Phys. 93 (1990) 552–561.

[13] U. Buck, I. Ettischer, M. Melzer, V. Buch, J. Sadlej, Phys. Rev. Lett. 80 (1998) 2578–2581.

[14] D.C. Clary, D.M. Benoit, J. Chem. Phys. 111 (1999) 10559–10565.

[15] A.R. Walton, D.E. Manolopoulos, Mol. Phys. 87 (1996) 961–978.

[16] K. Thompson, N. Makri, Phys. Rev. E 59 (1999) R4729–R4732.

[17] K.G. Kay, J. Chem. Phys. 101 (1994) 2250–2260.

[18] M.F. Herman, E. Kluk, Chem. Phys. 91 (1984) 27.

[19] E.J. Heller, J. Chem. Phys. 62 (1975) 1544.

[20] S. Garashchuk, F. Grossmann, D. Tannor, J. Chem. Soc. Faraday Trans. 93 (1997) 781–789.

[21] W.H. Miller, Adv. Chem. Phys. 30 (1975) 77.

[22] X. Sun, W.H. Miller, J. Chem. Phys. 108 (1998) 8870–8877.

[23] D. Neuhauser, J. Chem. Phys. 93 (1990) 2611–2616.

[24] J.W. Pang, T. Dieckmann, J. Feigon, D. Neuhauser, J. Chem. Phys. 108 (1998) 8360–8368.

[25] E. Narevicius, D. Neuhauser, H.J. Korsch, N. Moiseyev, Chem. Phys. Lett. 276 (1997) 250–254.

[26] M.R. Wall, D. Neuhauser, J. Chem. Phys. 102 (1995) 8011–8022.

[27] V.A. Mandelshtam, H.S. Taylor, Phys. Rev. Lett. 78 (1997) 3274–3277.

[28] V.A. Mandelshtam, J. Chem. Phys. 108 (1998) 9999–10007.

[29] R.Q. Chen, H. Guo, Chem. Phys. Lett. 308 (1999) 123–130.

[30] M.H. Beck, H.D. Meyer, J. Chem. Phys. 109 (1998) 3730–3741.

[31] F. Grossmann, V.A. Mandelshtam, H.S. Taylor, J.S. Briggs, Chem. Phys. Lett. 279 (1997) 355–360.

[32] R. Roy, B.G. Sumpter, G.A. Pfeffer, S.K. Gray, D.W. Noid, Phys. Reports – Rev. Section Phys. Lett. 205 (1991) 109–152.

[33] A. Bach, S. Leutwyler, D. Sabo, Z.J. Bacic, Chem. Phys. 107 (1997) 8781.

[34] R. Kosloff', J. Phys. Chem. 92 (1988) 2087.

[35] N. Moiseyev, private communication.