

Imaginary Vibrational Modes in Polycyclic Aromatic Hydrocarbons: A Challenging Test for the Hardness Profiles

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In a very recent article (J. Am. Chem. Soc. 2006, 128, 9342–9343) Moran et al. found that electron-correlated methodologies using popular Pople basis sets lead to spurious nonplanar polycyclic aromatic hydrocarbon (PAH) equilibrium structures. Furthermore, some of the present authors have shown that the hardness profiles along a reaction path can be a useful tool to find spurious stationary points in the potential energy surface. Herein, we test

the performance of the hardness profiles to detect shortcomings in energy profiles for the challenging case of nonplanar PAHs. The results obtained show that in 41 of the 42 imaginary vibrational modes studied, the hardness profiles indicate the wrong number and type of the potential energy surface stationary points.

Introduction

In the last decades, quantum chemistry has become a useful and powerful tool which has been largely used for characterizing and interpreting molecular structures and chemical reactions in a wide range of fields (chemistry, biochemistry, and nanotechnology).^[1] The cornerstone of the ab initio quantum chemistry methodologies is the Hartree–Fock theory, where each electron moves in an average electric field created by the nuclei and by all of the other electrons. However, for accurate studies of molecular systems it is necessary to use post-Hartree–Fock methods in order to take into account the effects of dynamical correlation [e.g. Møller–Plesset (MP),^[2] configuration-interaction (CI),^[3] coupled-cluster (CC)^[4] approaches] and/or non-dynamical correlation [e.g. multiconfigurational self-consistent field (MSCF)^[5]]. A very popular alternative to the conventional ab initio post-Hartree–Fock methods is the density functional theory (DFT).^[6] DFT has been proved to be a versatile way to include dynamical and non-dynamical electron correlation at a much lower computational cost than the usual post-Hartree–Fock methods.

An enormous amount of effort has been devoted to develop mathematical and computational techniques to improve the accuracy and implementation of these ab initio and DFT methodologies in the standard quantum program packages. Despite all this progress, there are still difficulties to properly describe reactions with weak inter and/or intramolecular interactions, where the incorrect selection of the basis set and/or methodology can produce changes in the number and/or the nature of the stationary points of the potential energy surfaces (PES).^[7] For these pathological systems the use of accurate and expensive ab initio calculations is requested [e.g. CCSD(T)/aug-cc-pVTZ], although computing requirements become prohibitively expensive for applications to large systems.

Another interesting and unexpected example of these pathological systems has been recently reported by Moran

et al.,^[8] who have found that the electron-correlated MP2, MP3, CISD, and CCSD methodologies using popular Pople basis sets lead to nonplanar polycyclic aromatic hydrocarbon (PAH) equilibrium structures. The spurious imaginary vibrational frequencies of the corresponding planar structures are out-of-plane (OOP) bending frequencies, which for the case of benzene yield D_{3d} chair and/or C_{2v} boat equilibrium geometries more stable than the D_{6h} planar structure. Moran et al.^[8] concluded that these imaginary vibrational frequencies arise from an intramolecular basis set incompleteness error (BSIE) due to the imbalance of the number of s, p, or even d functions with respect to the number of higher angular momentum functions (in special carbon f shells). The results of Moran et al. are in perfect agreement with the data obtained by Saeki, Akagi, and Fujii,^[9] who have shown that geometry optimizations of naphthalene at the MP2 level with 6-31G, 6-31G*, 6-31+G*, and 6-311G basis sets lead to a nonplanar geometry. On the contrary, naphthalene has a planar equilibrium geometry when the 6-31G*(0.25) or Dunning's correlation-consistent basis sets are used.

In recent studies^[10] some of the present authors have shown that the hardness profiles along a reaction path are less dependent on the method and basis set used than the energy pro-

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files. This fact has been checked for a series of well-known chemical processes for which the choice of a wrong methodology and/or basis set results in the presence of spurious stationary points in the PES; that is, the number and/or type (minimum or saddle point) of stationary points are wrong.^[10] On the contrary, the spurious stationary points were not present in the hardness profiles.^[10,11] Furthermore, the basis set superposition error (BSSE) of the energy and hardness profiles has been evaluated by means of the chemical Hamiltonian approach.^[12] The contrast of the energy and hardness profiles with and without BSSE for the hydrogen fluoride dimer corroborates that the hardness profiles are less dependent on the BSSE than the energy profiles.^[11] This suggests that the hardness profile can be used as a tool to check the presence of spurious stationary points on the PES,^[10,11] particularly for those systems that cannot be studied with accurate methodologies because of their size.

The main goal of the present work is to check the reliability of the hardness profiles to detect wrong energy profiles in the challenging case of pathological behavior of the electron-correlated methodologies when a basis set without higher angular momentum functions is used to predict the equilibrium geometry of PAHs. For this purpose, we have chosen the 9 PAHs studied by Moran et al.^[8] (see Figure 1). In the present paper we present the energy and hardness profiles for the imaginary vibrational OOP modes obtained using the MP2 methodology and three of the problematic Pople basis sets used by Moran et al.,^[8] that is, 6-311G, 6-311++G, and 6-311++G(d,p).

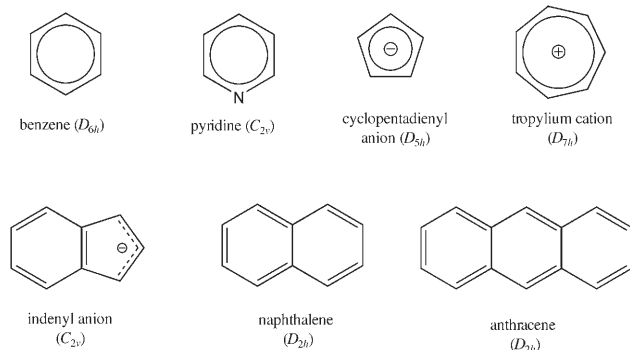


Figure 1. A schematic representation of the nine PAHs studied in this work.

Theory and Computational Details

Pearson^[13] defined the hardness as a measure of the resistance of a chemical species to change its electronic configuration. The analytical definition of the hardness was given by Parr and Pearson^[14] in the framework of the conceptual DFT^[15] as shown in Equation (1)

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})}, \quad (1)$$

where $v(\vec{r})$ is the potential acting on an electron at \vec{r} due to the nuclear attraction plus such other external forces as may be present, for example, an electric or a magnetic field. Applying the finite

difference approximation to Equation (1), one obtains Equation (2):

$$\eta_1 = I - A, \quad (2)$$

where I and A are the first vertical ionization potential, that is, $E(N-1) - E(N)$, and electron affinity, that is, $E(N) - E(N+1)$, respectively. The previous formula can be further simplified to Equation (3) if Koopmans' theorem^[16] is applied:

$$\eta_2 = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}, \quad (3)$$

where $\varepsilon_{\text{HOMO}}$ and $\varepsilon_{\text{LUMO}}$ are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. The expressions given by Equations (2) and (3) are the two most used operational hardness formulas.

The hardness definition given by Equation (1) has been used to rationalize two fundamental chemical reactivity principles: the hard and soft acids and bases (HSAB)^[13,17] and the maximum hardness principle (MHP).^[13,18] According to the MHP, the systems tend to a state of maximum hardness at constant temperature, external potential, and chemical potential.^[13,18] Even though these constraints are never fulfilled in any kind of nuclear displacement, the literature has shown that the relaxation of these constraints is permissible and it has been found that the MHP holds for molecular vibrations,^[19–21] internal rotations,^[22] and different types of chemical reactions.^[23] However, some failures of the MHP have also been reported,^[24] with hardness profiles violating the MHP. Thus, hardness profiles can follow or break the MHP, but in both cases the stationary points of the hardness profiles are usually very close to the stationary points of the energy profiles.

The geometry optimizations and frequencies of the nine PAHs studied in this work have been performed at the MP2 level using three Pople basis sets^[25] [6-311G, 6-311++G, and 6-311++G(d,p)]. The energy and hardness profiles have been evaluated along all the imaginary vibrational frequencies. These profiles have been evaluated with twenty positive displacements about the planar equilibrium geometry along the imaginary vibrational frequency mode. The displacements values are $0.01 \times n$ a.u., where n is a natural number from 1 to 20. It is worth noting that this linear transit path is an approximation of the intrinsic reaction path (IRP), although it correctly describes the existence of the spurious non-planar minima in the energy profiles for all the studied cases with just one exception. This unique exception is the smallest imaginary frequency ($150.2i \text{ cm}^{-1}$) of the 42 imaginary frequencies presented in Table 1, corresponding to a b_{2g} mode of naphthalene computed at the MP2/6-311++G(d,p) level.

It is worth noting that in the energy and hardness profiles only the positive distortions with respect to the equilibrium geometry are displayed. As the nontotally symmetric normal modes break the symmetry of the configuration of the nuclei, the symmetric configurations must be stationary points of both potential and hardness profiles. The positive and negative displacements of the nondegenerate nontotally symmetric normal modes yield molecular configurations that have the same energy and hardness.^[19] On the contrary, if the displacements are performed along one degenerate normal mode (e.g. e_{2u} , e_2'' , and e_1'') the positive and negative displacements yield molecular geometries that can have different values of energy and hardness. We have avoided this problem by averaging the energy and hardness obtained from the displacements of both degenerate modes. Nevertheless, it is important to remark that the conclusions of this work are the same if the averaging is not performed.

The calculations have been done within the restricted formalism except for open-shell systems, where the unrestricted approach has been followed. All the energy and hardness calculations have been carried out with the Gaussian 03 package.^[26]

Results and Discussion

Table 1 contains the summary of the 42 imaginary vibrational frequencies obtained for the 9 PAHs studied in this work using the MP2 methodology and the 6-311G, 6-311++G, and 6-311++G(d,p) basis sets. The hardness profile as a tool to detect spurious energy profiles can be applied for any nontotally symmetric distortions. However, in the present work we will only focus on the challenging imaginary vibrational frequencies. Next to each vibrational value it is also indicated if the hardness profiles follow or break the MHP. Fulfilling the MHP implies that the energy and hardness profiles display opposite behavior; that is, a minimum and a maximum of hardness will be located near a maximum and a minimum of energy, respectively. In contrast, a breakdown of the MHP implies that the hardness and energy shapes present parallel tendencies; that is, a minimum and a maximum of hardness will be located near a minimum and a maximum of energy, respectively.

Figure 2a contains the energy and hardness profiles along the b_{2g} 723 cm^{-1} vibrational mode of benzene evaluated at the MP2/6-311G level (as has been noted in the previous section, only the positive distortions with respect to the equilibrium geometry are displayed). As one can see, the energy profile shows two spurious stationary points: a maximum and a mini-

um of energy at the D_{6h} and nonplanar geometries, respectively. Otherwise, the hardness profiles (η_1 and η_2) only display one stationary point at the D_{6h} geometry. The lack of correspondence between the number of stationary points in the hardness and energy profiles is an indication of the incorrectness of the energy profile. At this point it is important to remark that, as has previously been noted, all energy and hardness profiles along a nontotally symmetric normal mode will always show a stationary point at zero displacement.^[21,27]

The energy profile used as reference to decide if a mode is MHP or anti-MHP was the correct one with only a minimum of energy at zero displacement. Figure 2a shows that the hardness profiles have a maximum at zero displacement. Then, following this criteria the MP2/6-311G b_{2g} 723 cm^{-1} vibrational mode of benzene fulfills the MHP.

In 41 of the 42 studied cases the η_1 profiles indicate the existence of the spurious nonplanar minimum along the imaginary vibrational modes, showing the trustworthiness of the hardness profiles to check the reliability of the PES. The only failure of the η_1 profile is the a_2 485.5 cm^{-1} vibrational mode of the indenyl anion evaluated at the MP2/6-311G level, which will be discussed in detail at the end of this section. In addition, it is important to remark that η_2 ($\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$) always mimics the shape of η_1 ($I - A$) with the only exception of the b_{2g} 1031.7 cm^{-1} vibrational mode of naphthalene evaluated at the MP2/6-311++G(d,p) level (see Figure 6i in the Supporting Information). In this case η_2 has two stationary points whereas η_1 has only one indicating the incorrect behavior of the energy profile. Despite the similarity between the η_1 and η_2 profiles, in the present work we will only focus on the η_1 profiles, because

the approximation of η_2 is based on the Hartree–Fock methodology (HOMO and LUMO energies) which correctly describes the planarity of the PAHs. Then, the correct profiles obtained using η_2 are not unexpected. However, it is far more surprising that using η_1 one also obtains the correct hardness profiles, although this approximation is based on the MP2 energy profiles showing the wrong number and type of stationary points.

To analyze in more detail the origin of the correct shape of the η_1 hardness profiles in Figure 3a we show the energy profiles of benzene with N , $N+1$, and $N-1$ electrons (N being the neutral case) along the b_{2g} 723.4 cm^{-1} vibrational mode calculated at the MP2/6-311G level. The three profiles show parallel tendencies with a spurious maximum and a spurious minimum of energy at the D_{6h} and nonpla-

Table 1. Summary of the imaginary vibrational frequencies (cm^{-1}) studied in this work.^[a]

Molecule	MP2/6-311G	MP2/6-311++G	MP2/6-311++G(d,p)
benzene (D_{6h})	b_{2g} 723.4i MHP *	b_{2g} 1852.1i MHP × e_{2u} 467.9i MHP ×	b_{2g} 1190.6i MHP ×
pyridine (C_{2v})	–	–	b_1 770.2i MHP ×
cyclopentadienyl anion (D_{5h})	e_2'' 400.8i MHP ×	e_2'' 866.9i MHP × e_1'' 255.7i MHP ×	e_2'' 198.0i MHP ×
tropylium cation (D_{7h})	–	e_2'' 1034.8i MHP *	e_2'' 538.3i MHP *
indenyl anion (C_{2v})	a_2 1118.7i MHP * b_1 582.5i MHP * a_2 485.5i MHP × b_1 251.6i MHP * a_2 167.0i MHP ×	a_2 1436.7i MHP × b_1 1009.4i MHP × a_2 902.5i MHP × b_1 603.9i MHP × a_2 486.8i MHP × a_2 166.0i MHP ×	a_2 780.2i MHP × b_1 395.4i MHP × a_2 240.2i MHP ×
naphthalene (D_{2h})	b_{2g} 1409.7i MHP * a_u 656.6i MHP * b_{3u} 366.8i MHP *	b_{2g} 1833.1i MHP × a_u 1264.7i MHP × b_{2g} 805.1i MHP × b_{3u} 764.9i MHP × b_{1g} 345.6i MHP ×	b_{2g} 1031.7i MHP × a_u 667.6i MHP × b_{2g} 150.2i MHP ×
anthracene (D_{2h})	b_{2g} 1649.6i MHP * a_u 1255.2i MHP * b_{2g} 606.5i MHP * b_{3u} 570.5i MHP * b_{1g} 339.5i MHP * a_u 305.5i MHP *	[b]	[b]

[a] MHP * and MHP × indicate that the hardness profiles follow and break, respectively, the MHP with respect to the correct energy profile without spurious stationary points. [b] Values not calculated because of computational requirements.

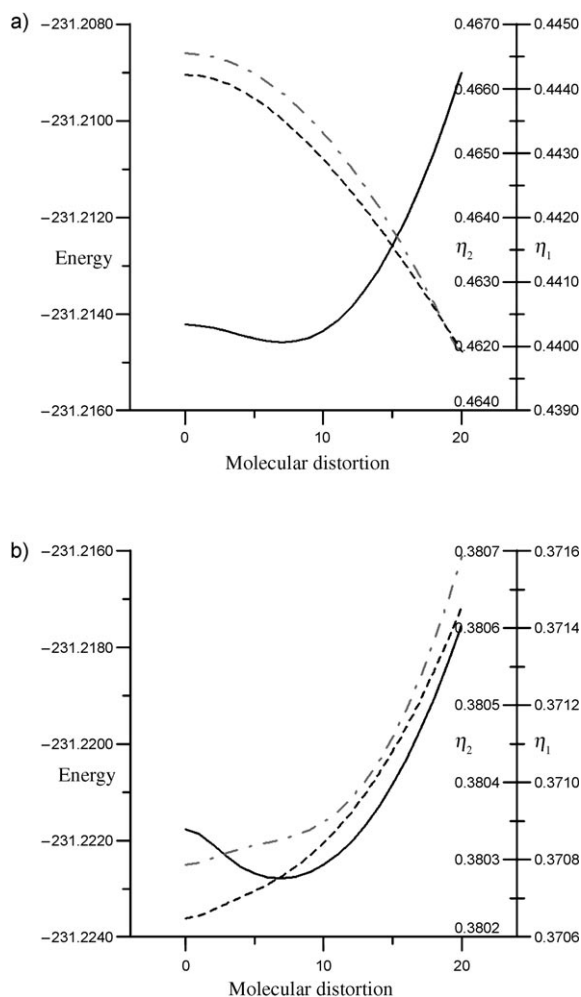


Figure 2. Energy (—) and hardness η_1 (---) and η_2 (-·-·) profiles calculated for molecular distortions of benzene along the vibrational modes a) 723.4i cm⁻¹ b_{2g} at the MP2/6-311G level and b) 1852.1i cm⁻¹ b_{2g} at the MP2/6-311++G level. The energy and hardness values are given in a.u.

nar geometries, respectively. In contrast, the differences between these energies, I and A , show convex increasing curves (see Figure 4a), resulting in a profile with only one stationary point at the D_{6h} geometry. As has been argued by Moran et al.,^[8] the nonplanarity of the PAHs calculated by the electron-correlated methodologies is due to an imbalance of the number of s , p , or even d functions with respect to the number of higher angular momentum functions. Then, it is reasonable to assume that the energy of the N , $N+1$, and $N-1$ electron systems would show a similar intramolecular basis set incompleteness error. As a result, the differences of these energies produce a cancellation of most of the BSIE, finally resulting in a nearly BSIE-free hardness profile. Equivalent graphs to Figure 3a are obtained for the majority of the remaining imaginary nontotally symmetric normal mode profiles.

Table 1 shows that for some vibrational modes the tendency to follow or break the MHP changes when the basis set is changed. For instance, at MP2/6-311G the displacements along the spurious b_{2g} vibrational mode follow the MHP, whereas at

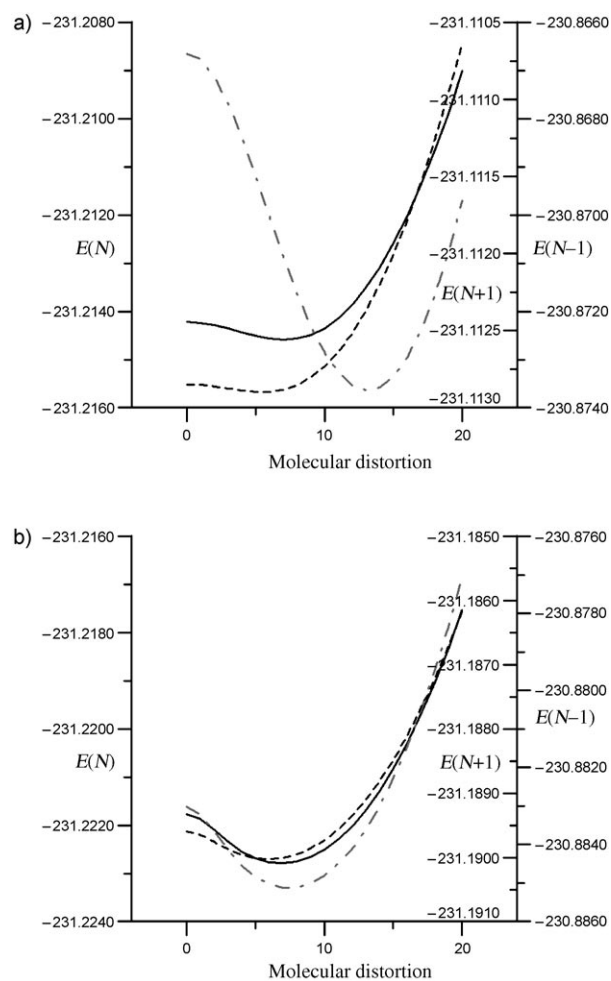


Figure 3. Energy profiles for benzene neutral (N , —), cation ($N-1$, ---), and anion ($N+1$, -·-·) calculated for distortions along the vibrational modes a) 723.4i cm⁻¹ b_{2g} at the MP2/6-311G level and b) 1852.1i cm⁻¹ b_{2g} at the MP2/6-311++G level. The energy values are given in a.u.

MP2/6-311++G the same displacements break the MHP. This different behavior can be understood looking at the symmetry of the LUMO orbitals and/or at the symmetry of the electronic states of the system with $N+1$ electrons, which might change from one basis set to another. However, as can be seen in Figures 3a and b the $E(N+1)$ profiles of the two electronic states have two stationary points, as their $E(N)$ and $E(N-1)$ counterparts. Then, as seen in Figures 4a and b, although the MP2/6-311G η_1 profile is convex and the MP2/6-311++G η_1 profile is concave, both have a unique stationary point. Thus, the hardness profile is successful in indicating the incorrectness of PES even when the symmetry of electronic states obtained with $N+1$ and $N-1$ electrons changes with the level of calculation. The other E , η_1 , and η_2 profiles for the imaginary vibrational frequencies of Table 1 are provided in the Supporting Information.

Finally, we want to analyze the special case of the a₂ 485.5i cm⁻¹ vibrational mode of the indenyl anion. Figure 5 displays the failure of η_1 to predict the incorrectness of the energy profile. Both the energy and hardness profiles show two spurious

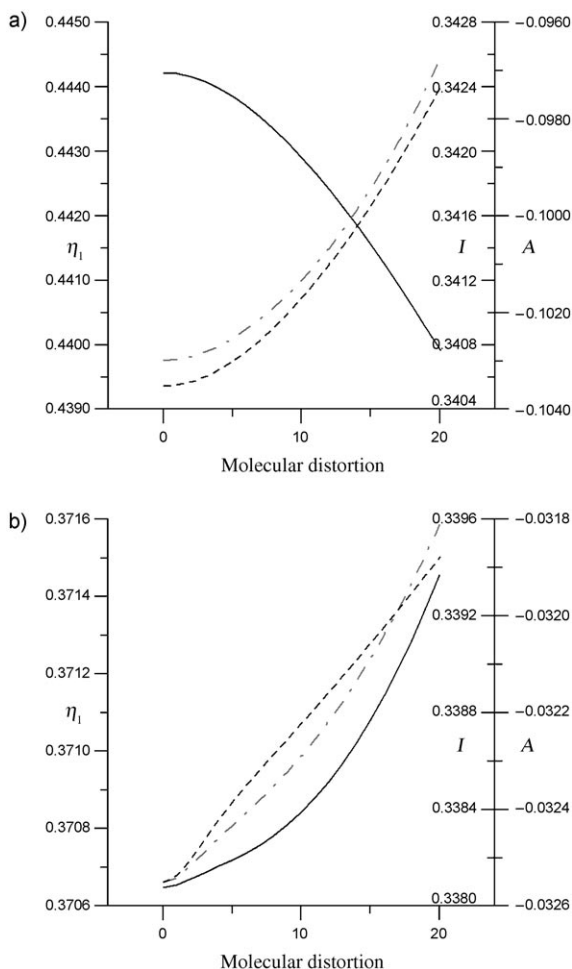


Figure 4. Profiles of the hardness η_1 (—), electron affinity A (---), and ionization potential I (-·-·-) calculated for the molecular distortions of benzene along the vibrational modes a) $723.4i \text{ cm}^{-1} b_{2g}$ at the MP2/6-311G level and b) $1852.1i \text{ cm}^{-1} b_{2g}$ at the MP2/6-311++G level. The hardness, electron affinity, and ionization potential values are given in a.u.

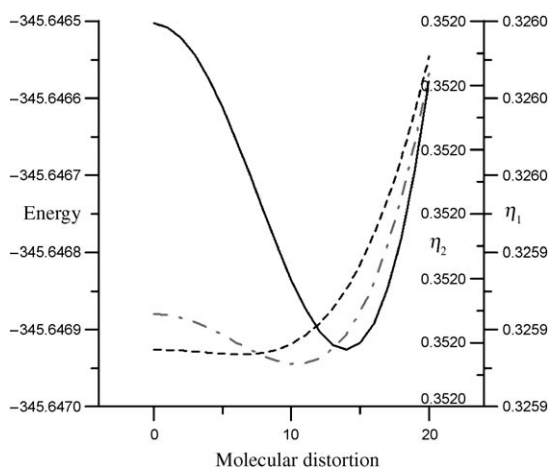


Figure 5. Energy (—) and hardness η_1 (---) and η_2 (-·-·-) profiles calculated for the molecular distortions of the indenyl anion along the vibrational mode $485.5i \text{ cm}^{-1} a_2$ evaluated at the MP2/6-311G level. The energy and hardness values are given in a.u.

stationary points along the vibrational mode. In Figure 6 we present the energy profiles along the imaginary frequency mode of the system with N , $N + 1$, and $N - 1$ electrons. In con-

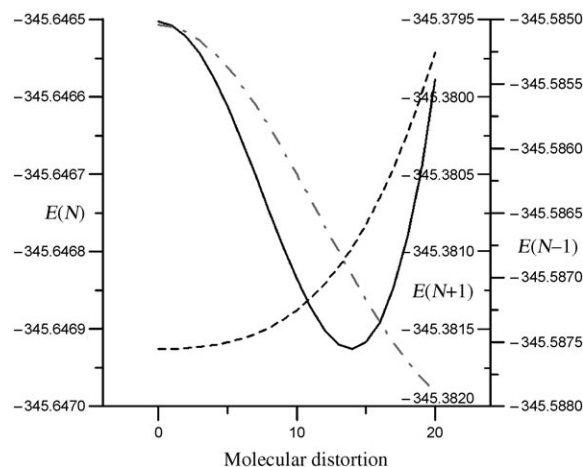


Figure 6. Profiles of the energies for the indenyl anion (N , —), neutral radical ($N-1$, ---), and double anion ($N+1$, -·-·-) calculated for distortions along the vibrational mode $485.5i \text{ cm}^{-1} a_2$ evaluated at the MP2/6-311G level. The energy values are given in a.u.

trast to the other 41 imaginary vibrational modes studied, the energy profile of the system with N electrons has a very different shape to the energy profiles of the system with $N + 1$ and $N - 1$ electrons. While in the first case the $E(N)$ profile presents two stationary points, the $E(N - 1)$ and $E(N + 1)$ profiles have only the zero displacement stationary point. Then, for this particular case the cancellation of the BSIE in the calculation of I and A profiles along the a_2 imaginary frequency vibrational mode would not be as effective as in the precedent cases.

Conclusions

In this work we have investigated the energy and hardness profiles along the imaginary vibrational modes of 9 PAHs at MP2 level using three different Pople basis sets [6-311G, 6-311++G, and 6-311++G(d,p)]. The hardness profiles calculated as the difference between the vertical ionization and electron affinity indicate the incorrectness of the energy surfaces in 41 of the 42 imaginary vibrational modes studied, showing the trustworthiness of the hardness profiles to check the reliability of the PES. In addition, we have shown that the energy profiles of the system with $N + 1$ and $N - 1$ electrons display similar tendencies than their counterpart of the system with N electrons, indicating similar BSIEs for the three profiles. Thus, the differences of these energies to evaluate I and A produce a cancellation of most of the BSIE, obtaining finally nearly BSIE-free hardness profiles. Hardness profiles can thus be a good methodology to perform a preliminary check of the reliability of the energy profiles, in particular for systems that due to their size (polymers and biomolecules) cannot be treated with accurate and expensive ab initio calculations. The hardness profile only requires the evaluation of n single-point calcula-

tions, where n or $3 \times n$ is the number of points in the profile depending on the use of the η_2 or η_1 approximations, respectively. One problem of η_1 is that the evaluation of $N + 1$ and $N - 1$ systems usually requires open-shell calculations, increasing the costs. For large systems the computation of the hardness profile with a low level of calculation will become incredibly cheaper than the evaluation of the vibrational frequencies with a higher level.

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- [1] A. Szabo, N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*, Macmillan, New York, **1989**; C. J. Cramer, *Essentials of Computational Chemistry*, Wiley, New York, **2002**; T. Helgaker, P. Jørgensen, J. Olsen, *Molecular Electronic-Structure Theory*, Wiley, Chichester, **2000**.
- [2] C. Möller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.
- [3] J. A. Pople, R. Seeger, R. Krishnan, *Int. J. Quantum Chem. Symp.* **1977**, *11*, 149–163.
- [4] J. Cizek, *Adv. Chem. Phys.* **1969**, *14*, 35–91; G. D. Purvis, R. J. Barlett, *J. Chem. Phys.* **1982**, *76*, 1910–1918; G. E. Scuseria, C. L. Janssen, H. F. Schaefer, *J. Chem. Phys.* **1988**, *89*, 7382–7387; G. E. Scuseria, H. F. Schaefer, *J. Chem. Phys.* **1989**, *90*, 3700–3703.
- [5] B. O. Roos, P. R. Taylor, *Chem. Phys.* **1980**, *48*, 157–173; K. Andersson, P. Å. Malmqvist, B. O. Roos, *J. Chem. Phys.* **1992**, *96*, 1218–1226; B. O. Roos, K. Andersson, M. P. Fulscher, P. Å. Malmqvist, L. Serrano-Andrés, K. Pierloot, M. Merchán in *Multiconfigurational Perturbation Theory: Applications in Electronic Spectroscopy*, Vol. 93, Wiley, New York, **1996**, pp. 219–331.
- [6] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**; W. Koch, M. C. Holthausen, *Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, **2000**.
- [7] D. Cremer, *J. Chem. Phys.* **1978**, *69*, 4440–4445; L. Turi, J. J. Dannenberg, *J. Phys. Chem.* **1993**, *97*, 7899–7909; S. Simon, M. Duran, J. J. Dannenberg, *J. Chem. Phys.* **1996**, *105*, 11024–11031; I. M. B. Nielsen, W. D. Allen, A. G. Csaszar, H. F. Schaefer, *J. Chem. Phys.* **1997**, *107*, 1195–1211; S. Re, Y. Osamura, Y. Suzuki, H. F. Schaefer, *J. Chem. Phys.* **1998**, *109*, 973–977; E. F. Valeev, H. F. Schaefer, *J. Chem. Phys.* **1998**, *108*, 7197–7201; P. Salvador, S. Simon, M. Duran, J. J. Dannenberg, *J. Chem. Phys.* **2000**, *113*, 5666–5674; Z. H. Li, K. N. Fan, *J. Phys. Chem. A* **2002**, *106*, 6659–6664; J. D. Larkin, K. L. Bhat, G. D. Markham, B. R. Brooks, H. F. Schaefer, C. W. Bock, *J. Phys. Chem. A* **2006**, *110*, 10633–10642; A. H. T. Li, S. D. Chao, *J. Chem. Phys.* **2006**, *125*, 94312–94318.
- [8] D. Moran, A. C. Simmonett, F. E. Leach, W. D. Allen, P. v. R. Schleyer, H. F. Schaefer, *J. Am. Chem. Soc.* **2006**, *128*, 9342–9343.
- [9] M. Saeki, H. Akagi, M. Fujii, *J. Chem. Theory Comput.* **2006**, *1*, 1176–1183.
- [10] M. Torrent-Sucarrat, J. M. Luis, M. Duran, M. Solà, *J. Chem. Phys.* **2004**, *120*, 10914–10924; M. Torrent-Sucarrat, M. Duran, J. M. Luis, M. Solà, *J. Chem. Sci.* **2005**, *117*, 549–554.
- [11] D. Asturiol, M. Duran, P. Salvador, M. Torrent-Sucarrat, *Int. J. Quantum Chem.* **2006**, *106*, 2910–2919.
- [12] I. Mayer, *Int. J. Quantum Chem.* **1983**, *23*, 341–363; I. Mayer, *Int. J. Quantum Chem.* **1998**, *70*, 41–63.
- [13] R. G. Pearson, *Chemical Hardness: Applications from Molecules to Solids*, Wiley, Oxford, **1997**.
- [14] R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516.
- [15] H. Chermette, *J. Comput. Chem.* **1999**, *20*, 129–154; P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.* **2003**, *103*, 1793–1873.
- [16] T. Koopmans, *Physica* **1934**, *1*, 104–113.
- [17] R. G. Pearson, *J. Chem. Educ.* **1987**, *64*, 561–567.
- [18] R. G. Parr, P. K. Chattaraj, *J. Am. Chem. Soc.* **1991**, *113*, 1854–1855; R. G. Pearson, *J. Chem. Educ.* **1999**, *76*, 267–275.
- [19] R. G. Pearson, W. E. Palke, *J. Phys. Chem.* **1992**, *96*, 3283–3285.
- [20] S. Pal, N. Vaval, R. Roy, *J. Phys. Chem.* **1993**, *97*, 4404–4406; P. K. Chattaraj, P. Fuentealba, P. Jaque, A. Toro-Labbé, *J. Phys. Chem. A* **1999**, *103*, 9307–9312.
- [21] G. Makov, *J. Phys. Chem.* **1995**, *99*, 9337–9339.
- [22] S. Gutiérrez-Oliva, J. R. Letelier, A. Toro-Labbé, *Mol. Phys.* **1999**, *96*, 61–70; T. Uchimaru, A. K. Chandra, S. Kawahara, K. Matsumura, S. Tsuzuki, M. Mikami, *J. Phys. Chem. A* **2001**, *105*, 1343–1353; P. K. Chattaraj, S. Gutiérrez-Oliva, P. Jaque, A. Toro-Labbé, *Mol. Phys.* **2003**, *101*, 2841–2853; J. Cadet, A. Grand, C. Morell, J. R. Letelier, J. L. Moncada, A. Toro-Labbé, *J. Phys. Chem. A* **2003**, *107*, 5334–5341; S. Gutiérrez-Oliva, A. Toro-Labbé, *Chem. Phys. Lett.* **2004**, *383*, 435–440.
- [23] D. Datta, *J. Phys. Chem.* **1992**, *96*, 2409–2410; T. K. Ghanty, S. K. Ghosh, *J. Phys. Chem.* **1996**, *100*, 12295–12298; P. K. Chattaraj, P. Fuentealba, B. Gómez, R. Contreras, *J. Am. Chem. Soc.* **2000**, *122*, 348–351; P. Jaque, A. Toro-Labbé, *J. Phys. Chem. A* **2000**, *104*, 995–1003; P. Jaque, A. Toro-Labbé, *J. Chem. Phys.* **2002**, *117*, 3208–3218; T. K. Ghanty, S. K. Ghosh, *J. Phys. Chem. A* **2002**, *106*, 4200–4204.
- [24] L. T. Nguyen, T. N. Le, F. De Proft, A. K. Chandra, W. Langenaeker, M. T. Nguyen, P. Geerlings, *J. Am. Chem. Soc.* **1999**, *121*, 5992–6001; L. T. Nguyen, F. De Proft, M. T. Nguyen, P. Geerlings, *J. Org. Chem.* **2001**, *66*, 4316–4326; M. Torrent-Sucarrat, J. M. Luis, M. Duran, M. Solà, *J. Am. Chem. Soc.* **2001**, *123*, 7951–7952; M. Torrent-Sucarrat, J. M. Luis, M. Duran, M. Solà, *J. Chem. Phys.* **2002**, *117*, 10561–10570; L. Blancafort, M. Torrent-Sucarrat, J. M. Luis, M. Duran, M. Solà, *J. Phys. Chem. A* **2003**, *107*, 7337–7339; M. Torrent-Sucarrat, J. M. Luis, M. Solà, *Chem. Eur. J.* **2005**, *11*, 6024–6031; M. Torrent-Sucarrat, M. Duran, J. M. Luis, M. Solà, *J. Phys. Chem. A* **2005**, *109*, 615–621; M. Torrent-Sucarrat, M. Solà, A. Toro-Labbé, *J. Phys. Chem. A* **2006**, *110*, 8901–8911; S. Noorizadeh, H. Maimhami, *J. Mol. Struct. (TheoChem)* **2006**, *779-800*, 133–144; J. Lahsen, J. Ramos-Grez, *J. Fluorine Chem.* **2006**, *127*, 373–376; Y. L. Zhang, Z. Z. Yang, *Int. J. Quantum Chem.* **2006**, *106*, 1723–1735.
- [25] W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.
- [26] Gaussian 03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.
- [27] A. K. Chandra, T. Uchimaru, *J. Phys. Chem. A* **2001**, *105*, 3578–3582.

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