Basis set effects on the energy and hardness profiles of the hydrogen fluoride dimer

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Abstract:

In a previous work, the present authors have shown that the hardness profiles are less dependent on the level of calculation than the energy profiles for potential energy surfaces (PESs) having pathological behaviors. At variance with energy profiles, hardness profiles always show the correct number of stationary points. This characteristic has been used to indicate the existence of spurious stationary points on the PESs. In the present work, we apply this methodology to the hydrogen fluoride dimer, a classical difficult case for the density functional theory methods.

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1. Introduction

The concept of Potential Energy Surface (PES) for molecules stems from the Born-Oppenheimer approximation for the separation of the nuclear and electronic motion. The PES is a smooth function that gives how the potential energy varies as relative coordinates of the atomic nuclei involved in a chemical system are changed. For a nonlinear molecule, consisting of n atoms, the PES depends on $3n$-6 coordinates corresponding to the total number of internal degrees of freedom. Years of experience have proven that the notion of the PES is extremely powerful to analyze molecular structure, spectroscopy, and chemical reactivity. Indeed, the whole chemistry can be considered as a series of exercises on PESs.[1,2]

The characterization of the PES is normally accomplished by locating and characterizing the chemical relevant stationary points, *i.e.* minima and transition states, which normally implies an important computational effort. Moreover, not always is feasible to fully reproduce the experimental results. This is particularly true in the case of chemical reactions, where the number and/or nature of stationary points (minima or transition states) may change with the basis set and/or the method of calculation.[3-8] In these pathological systems, high level *ab initio* methods (not always computationally affordable) are required to be certain of the correctness of the calculated PES.

The contribution of the density functional theory (DFT)[9-10] in the knowledge of the PES has been very important. The nonlocal hybrids DFT methods provide results with accuracy comparable to or frequently even higher than results from *ab initio* correlated calculations and using less computer time. However, the DFT methods also show pathological behaviors, being the hydrogen fluoride (HF) dimer a classical example in the literature.[4-8]

Both experiment and high level calculations indicate that the HF dimer has a planar (C_s) equilibrium structure (see Figure 1). One HF molecule forms a nearly linear hydrogen bond to the other.[4,5] Moreover, the PES of HF dimer also contains a transition state with C_{2h} cyclic structure, that connects the two possible C_s minima.

(Figure 1 here)

It is also know that DFT methods in conjunction with small basis sets tend to predict the cyclic structure as the only stable structure on the PES.[6-8] This error can be solved when accounting for the basis set superposition error (BSSE) through the optimization process.[8]

In a recent article,[11] the present authors studied a series of well-established inter and intramolecular rearrangements, where the use of a weak methodology or a poor basis set results in the presence of spurious stationary points on the PESs. In that work, the hardness profiles were found to be less sensitive to the change of basis or/and method than the energy profiles. Furthermore, the hardness profiles always presented the correct number of stationary points. For these reasons, the present authors concluded that the hardness profiles could be useful to check the validity of the energy profiles that because of computational requirements can not be treated with high level *ab initio* methods.

The hardness is a measure of the resistance of a chemical species to change its electronic configuration.[12] The analytical definition of η was given by Parr and Pearson[13] in the framework of the conceptual DFT[14,15] as the second-order partial derivative of the total electronic energy, E, with respect to the total electron number of electrons, N, at a fixed external potential $v(\vec{r})$:

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

$v(\vec{r})$ is the potential acting on an electron at $\vec{r}$ due to the nuclear attraction plus such other external forces as may be present. Related to the hardness, there are two fundamental chemical reactivity principles: the hard and soft acids and bases (HSAB)[12] principle and the maximum hardness principle (MHP).[12,16,17]

The MHP affirms that systems tend to a state of maximum hardness at constant temperature, external potential, and chemical potential.[17] Despite these strict constraints are not followed in any kind of nuclear displacement, it has been found that this principle holds in molecular vibrations,[18] internal rotations,[19] and different types of chemical reactions,[20] although some failures have also been reported.[21,22] Gazquez et al.[23] demonstrated that, under conditions of constant chemical potential, the harness profile has a maximum (minimum) where the energy profile has a minimum (maximum). Although in a reaction profile the chemical potential is not constant, previous studies on hardness profiles[18-21] indicate that a stationary point of the hardness is usually located close to a stationary point of the PES.

In a reaction which follows the MHP, the minima and transition states of the PES will represent maxima and minima of the hardness profile, respectively, although they could not exactly coincide in the same locations. In contrast in a reaction which breaks the MHP, the maxima and minima of the hardness profiles are respectively found near to the transition states and minima of the PESs. Thus, the number of stationary points in the PESs and the hardness profiles usually become identical. Consequently, the presence of a different number of stationary points in the hardness

and energy profiles is an indication of the presence of spurious stationary points on the PESs of the chemical processes.

The aim of the present work is to present another example of this utility of the hardness profile. For this reason, we will evaluate the energy and hardness profiles for the HF dimer at B3LYP level using eight different standard basis sets.

2. Computational details

The finite difference approximation and the Koopmans' theorem[24] in the Eq. (1) lead the following working definitions of the hardness:

$$\eta_1 = I - A \qquad \text{and} \qquad (2)$$

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

where I and A are the first vertical ionization potential and electron affinity of the neutral molecule, respectively, and ε_{LUMO} and ε_{HOMO} are the energies of the low unoccupied molecular orbital and the high occupied molecular orbital, respectively.

To construct the PES of the HF dimer a linear transit path is chosen, which is obtained by freezing at differing values the ∠HFF angle and optimizing the rest of internal coordinates (see Figure 1). The negative and positive values of the ∠HFF angle in the Figures 2 and 3 are related to the ∠HFFH dihedral angles of 0º and 180º degrees, respectively. The nature of the stationary points has always been checked by computing the harmonic vibrational frequencies. At each optimized point of the linear transit path, the hardness and energy have been evaluated to depict their corresponding profiles. An alternative choice as linear transit path could be the intrinsic reaction path, IRP, although for chemical systems with weak intermolecular interactions like HF dimmer,

The geometry optimizations and hardness calculations have been performed with the B3LYP method[25] using a series of Pople standard basis sets.[26] The energies of the cationic and anionic doublet species, needed to obtain the vertical I and A, have been computed within the unrestricted methodology at the geometry of the neutral system. All these calculations have been carried out with the Gaussian 98 package.[27]

3. Results and discussion

The Figure 2 displays the E, η_1, and η_2 profiles for the linear transit path described by the $\angle HFF$ angle computed at the B3LYP level using the STO-3G, 3-21G, 6-31G, 6-31+G(d), 6-311++G, 6-311G(d,p), 6-311++G(d,p), and 6-311++G(3df,3pd) basis sets. The best ab initio estimates[7] of the potential energy profile show a minimum for a $\angle HFF$ angle of about 7º (experimental value of 10±6º)[5] and a transition state with cyclic structure (C_{2h}) of about 50º.[8] These two stationary points present an energy barrier of only 1.3 kcal/mol at the B3LYP/6-311++G(3df,3pd) level. This proper energy profile has been well reproduced by the 6-31+G(d), 6-311++G, 6-311++G(d,p), and 6-311++G(3df,3pd) basis sets. In contrast, the 3-21G, 6-31G, and 6-311G(d,p) PESs only present one spurious minimum at the C_{2h} cyclic structure, showing the well-known importance of the diffuse functions to accurately describe the hydrogen-bonded complex of the HF dimer.[4,8] Finally, the STO-3G PES predicts four stationary points instead of two. In contrast to the 3-21G and 6-31G basis sets, the STO-3G basis set characterizes the minimum at 5º. However, it fails at the cyclic structure, predicting a spurious minimum at about 42º and two false transition states very close to the C_{2h} geometry.

(Figure 2 here)

In contrast to the strong dependence of the PES on the basis set, the shape of the hardness is nearly independent of the basis set. Between the different basis sets, there are some important changes in the absolute values of the hardness, although their shapes along the linear transit path remain unchanged.

The $\eta_2(\varepsilon_{LUMO} - \varepsilon_{HOMO})$ profiles in Figure 2 for the eight basis sets studied present a minimum and a maximum at about -5° and 50°, respectively, indicating the existence of two stationary points in the PES. Thus, the difference between the number of stationary points of the energy and hardness profiles [in the STO-3G, 3-21G, 6-31G, and 6-311G(d,p) basis sets] denotes the presence spurious stationary points on the corresponding PESs. It is worth nothing that this intermolecular conformational change breaks the MHP, because the maximum and minimum of the hardness profile are respectively found near to the transition state and the minimum of the correct PES. This behavior can be understood by analyzing the variation of the HOMO and LUMO energies along the linear transit path. The maximum of hardness near to the cyclic structure is due to a larger stabilization of the HOMO energy and a destabilization of the LUMO energy, while the minimum structure presents the most unstable and stable HOMO and LUMO energies, respectively, along the rearrangement reaction. In contrast to previous cases,[22] the behavior of the HOMO and LUMO energies along the linear transit path can not be easily discussed from the changes in the shape of the orbitals.

The $\eta_1(I - A)$ profiles mimic the shape of the η_2 profiles, indicating the existence of two stationary points in the PESs with the only remarkable difference that the minimum of η_1 appears some degrees shifted to the left side, more or less at -15°.

However, there are two basis sets, 6-311++G(d,p) and 6-311++G(3df,3pd), which show the expected minimum (in the Figure 2g the minimum is very shallow), but then, the η_1 shape decreases creating a spurious maximum of hardness (see the zoom of Figures 2g and 2h). The problem of the η_1 profiles arises from the evaluation of the energy of the system with N-1 electrons, because for the $(HF)_2^+$ species there are two quasidegenerate electronic states ($^2A'$ and $^2A''$), with a crossing point in the middle of the linear transit path. Therefore, the correct calculation of the ionization potential of this dimer should be carried out using multiconfiguration methods. Despite this multiconfiguration character of the ionization potential energy, the η_1 profiles of the Figure 2 have always been calculated taking the most stable electronic state at the B3LYP level. Thus, the η_1 results should be viewed with some skepticism. Obviously, this problem could be overcome using a multiconfiguration method like MCSF, but this is out of the scope of this paper. In contrast, the neutral HF dimer shows HOMO and HOMO-1 orbitals close in energy, but along the linear transit path there is not an interchange of these orbitals. Therefore, in this case the η_2 profiles should be considered, in principle, of better-quality than the η_1 profiles.

4. Conclusions

In this work, we have studied the energy and hardness profiles for the hydrogen fluoride dimer using the B3LYP level and eight different basis sets. In an analogous manner to our previous work, we have found that the hardness profile is more basis set independent than the energy profile. Indeed, the shape of the hardness profile is qualitatively the same for all basis set analyzed, while the energy profile is wrong with the STO-3G, 3-21G, 6-31G, and 6-311G(d,p) basis sets. Therefore, we have confirmed that, for the hydrogen fluoride dimer, the hardness profiles can also be used to check the

validity of the energy profiles. Using the larger basis sets, the hardness calculated using the approximation $I - A$ (η_1) does not reproduce the shape of the $\varepsilon_{LUMO} - \varepsilon_{HOMO}$ (η_2). The η_1 profiles contain a spurious maximum of hardness, likely due to the multiconfiguration character of its N-1 electronic state.

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Figure Captions

Figure 1: A schematic representation of the linear transit path obtained by changing the ∠HFF angle in the HF dimer with their correct stationary points.

Figure 2: B3LYP profiles of the relative energies (solid line) and hardness (η_1 dotted-dashed line and η_2 dashed line) for the linear transit path described by the ∠HFF angle calculated with the basis sets: (a) STO-3G, (b) 3-21G, (c) 6-31G, (d) 6-31+G(d), (e) 6-311++G, (f) 6-311G(d,p), (g) 6-311++G(d,p), and (h) 6-311++G(3df,3pd). The hardness η_1 and η_2 are calculated from Eqs. (2) and (3), respectively. The hardness values and the relative energies are given in a.u.

Minimum C_s **TS** C_{2h}
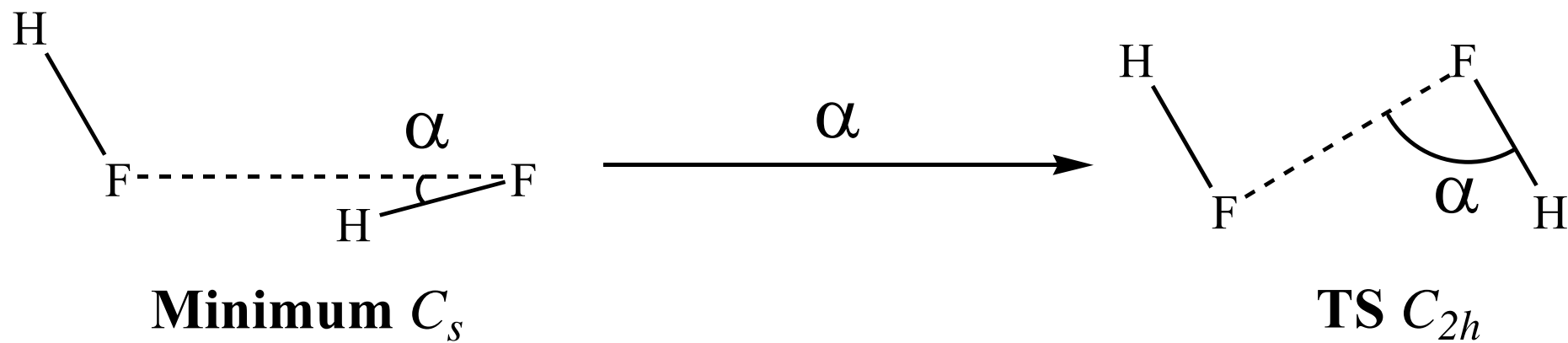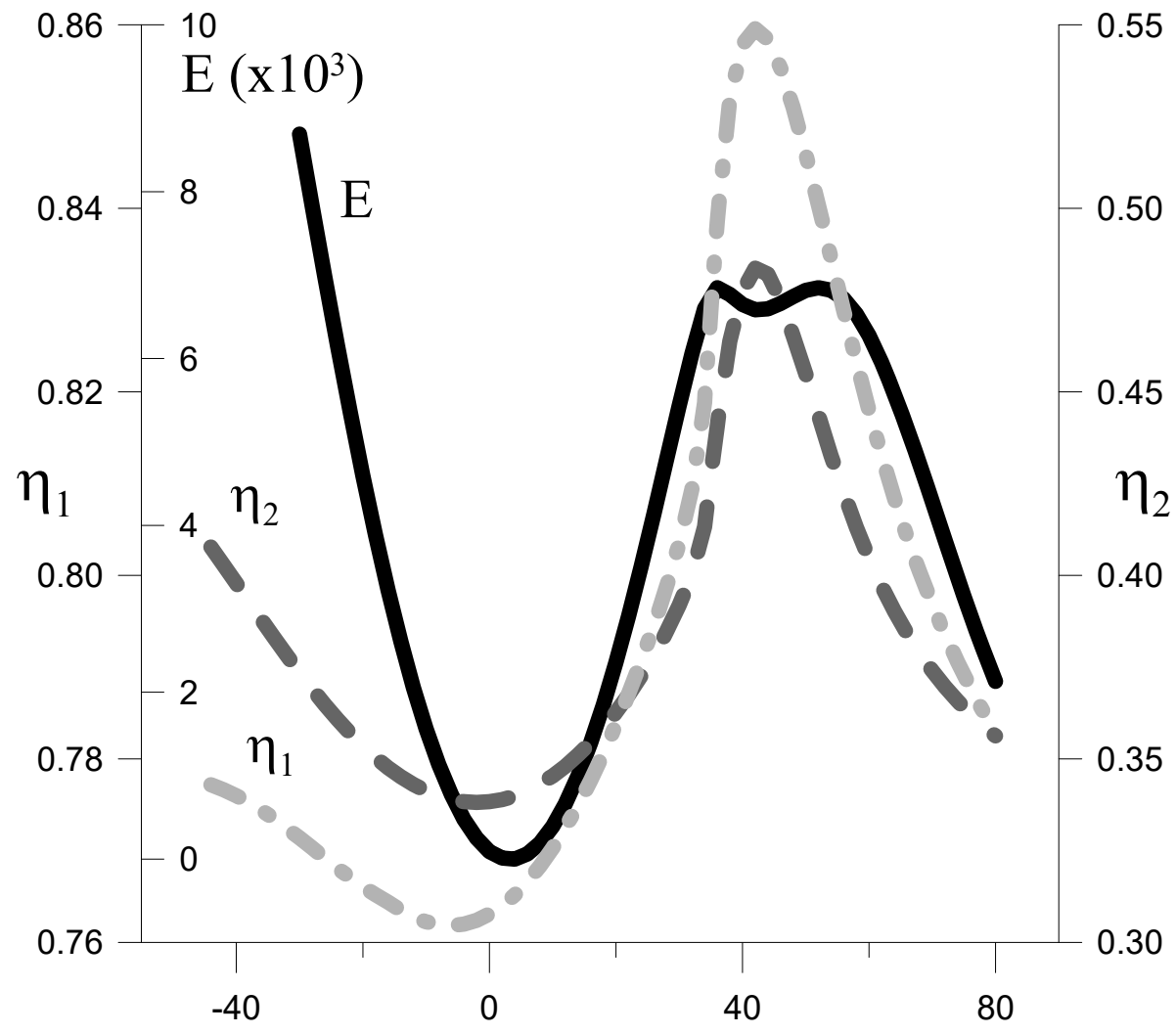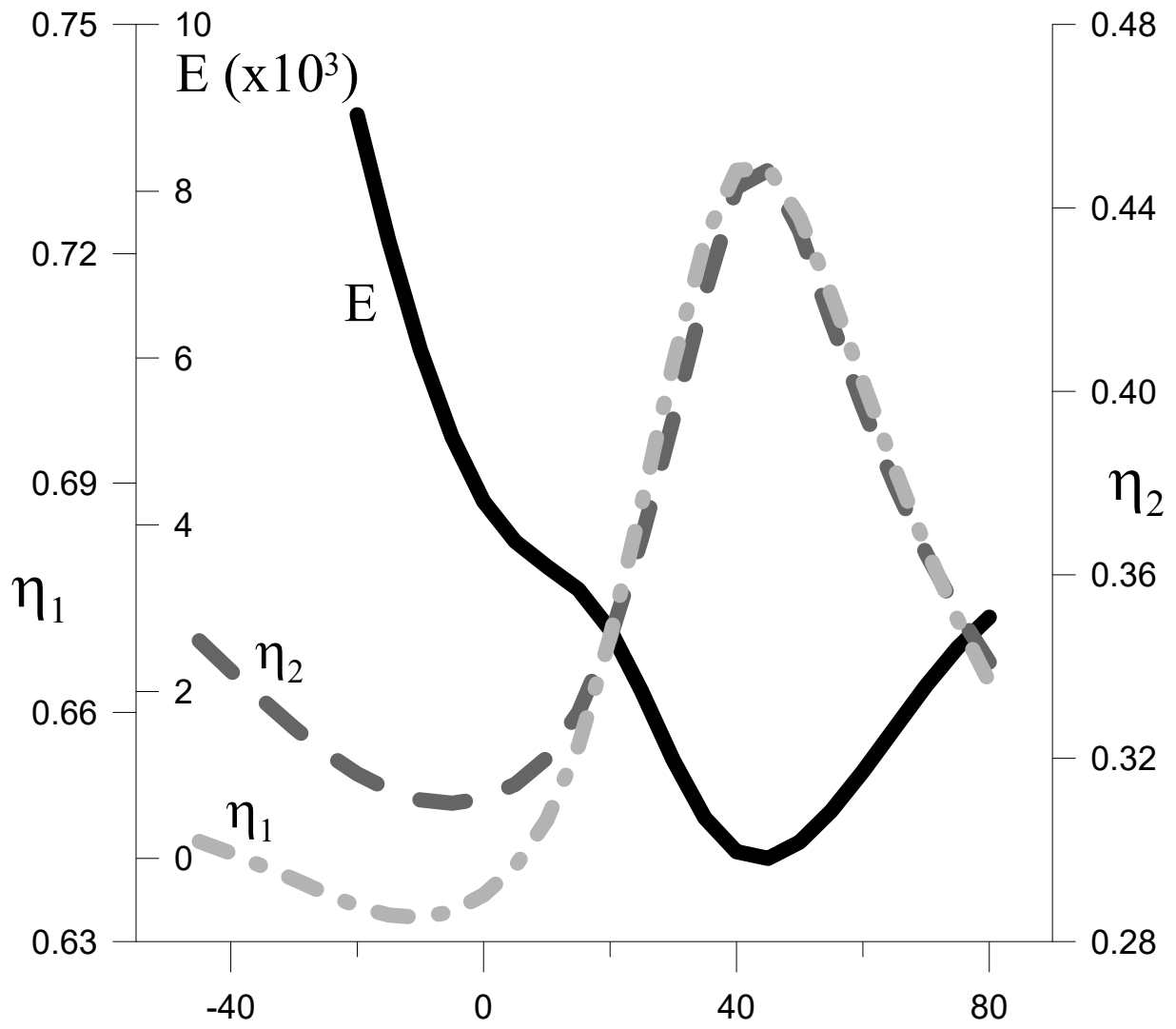
Figure 1

Figure 2a

Figure 2b
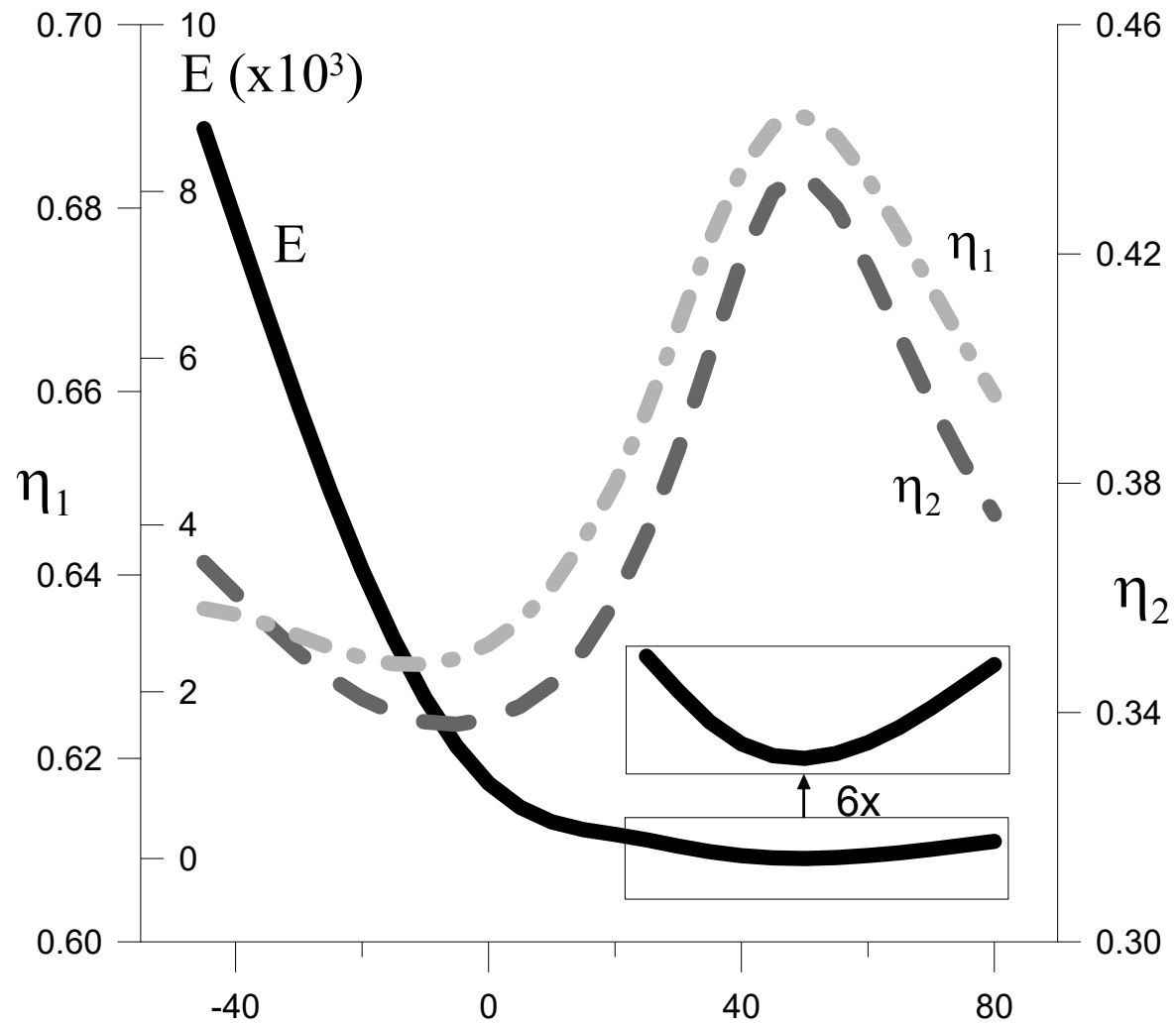
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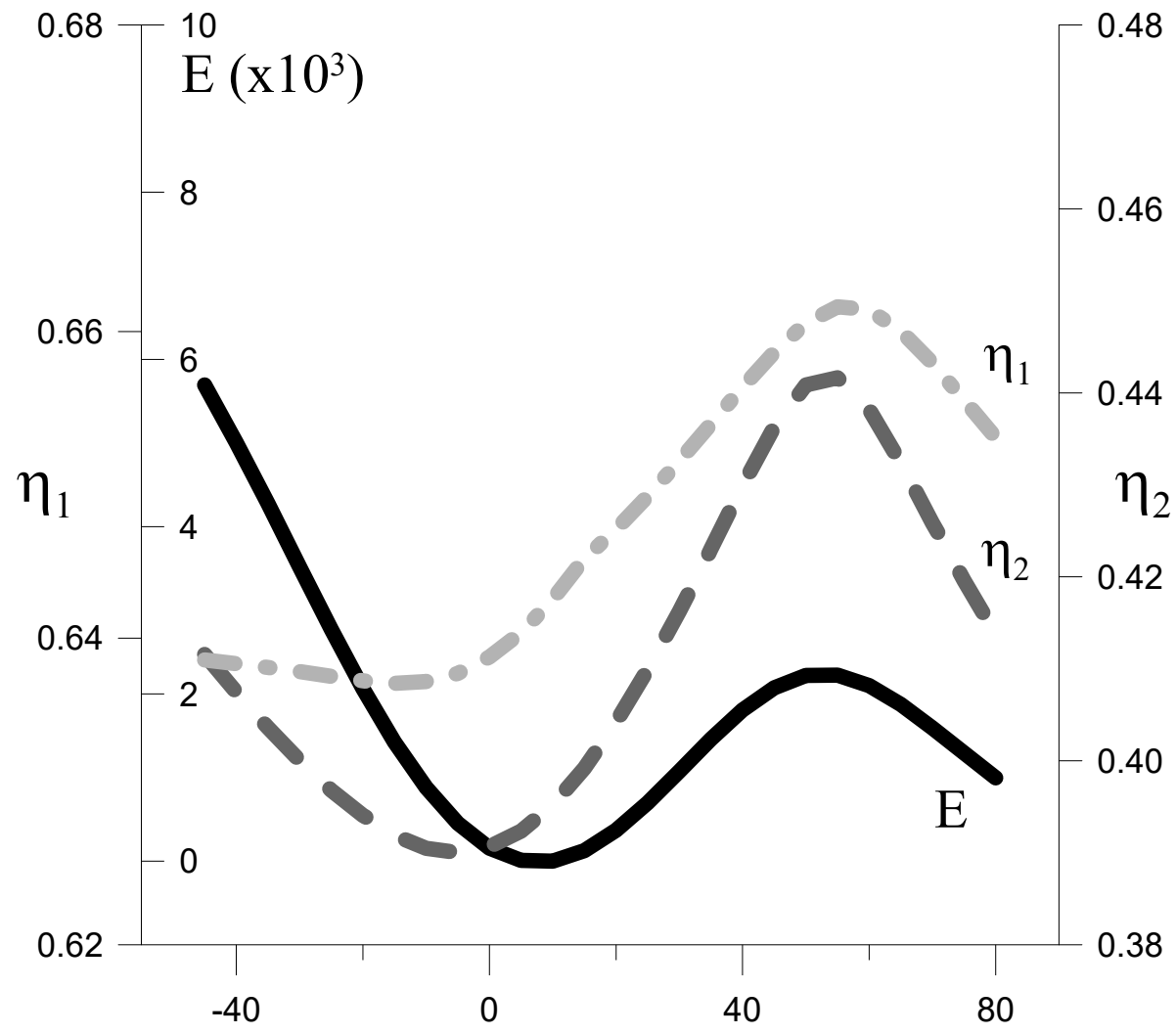
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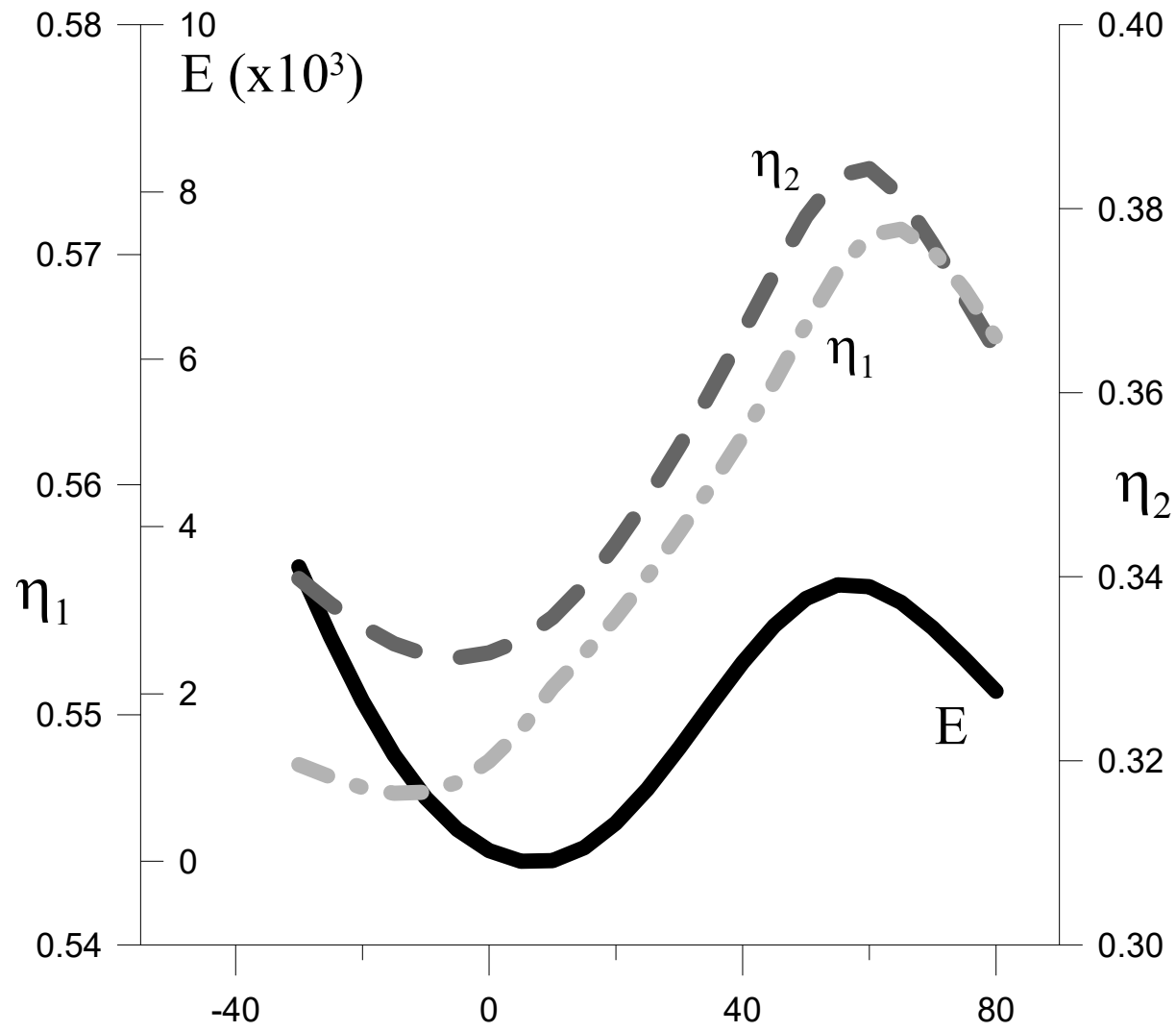
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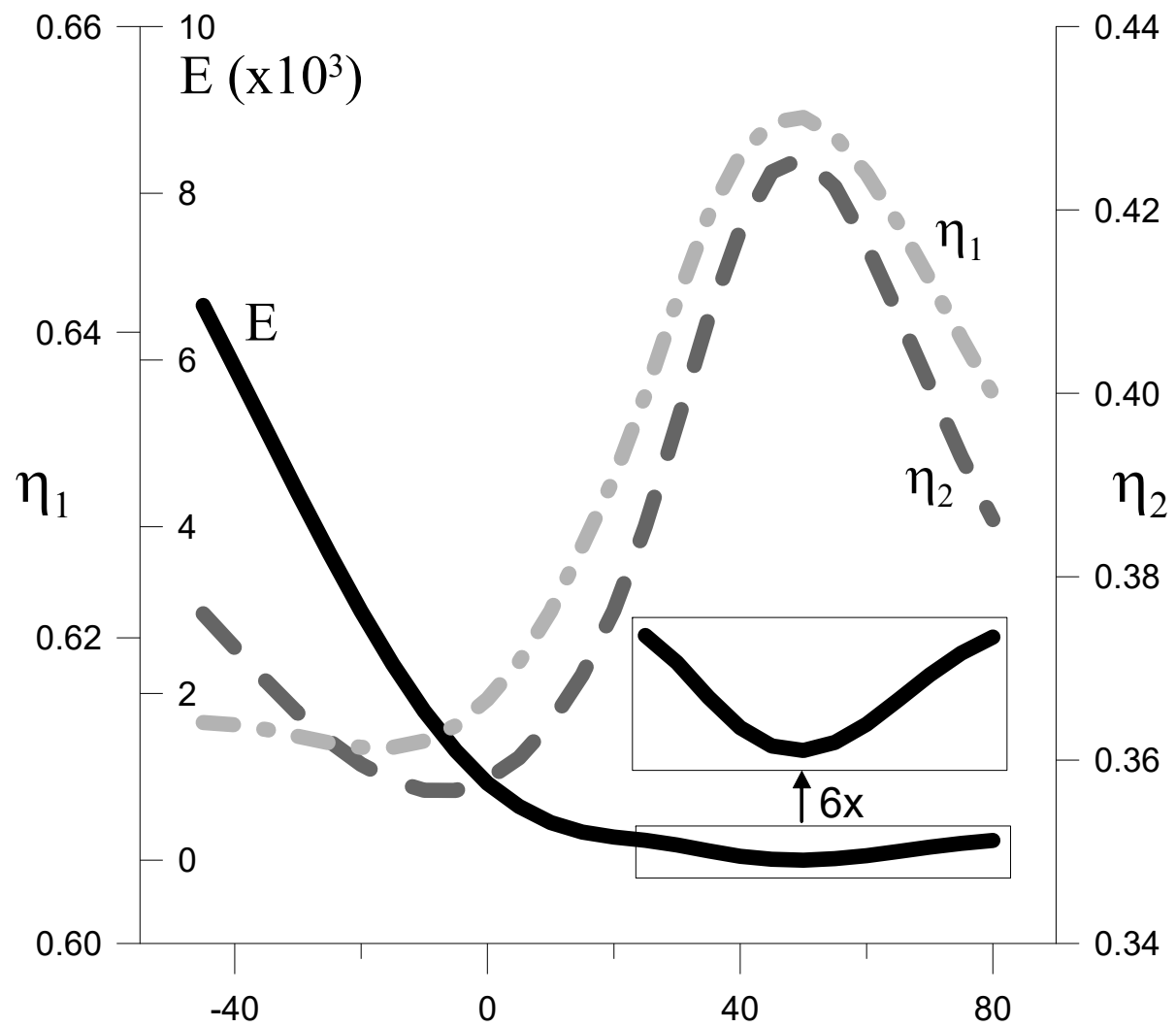
Figure 2f

Figure 2g

Figure 2h