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Potential Energy Surfaces for Vibrational Structure Calculations from a Multiresolution Adaptive Density-Guided Approach: Implementation and Test Calculations

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A multiresolution procedure to construct potential energy surfaces (PESs) for use in vibrational structure calculations is developed in the framework of the adaptive density-guided approach. The implementation of the method allows the construction of hybrid PESs with different mode-coupling terms calculated with a variety of combinations of electronic structure methods and basis sets. Furthermore, the procedure allows the construction of hybrid PESs that incorporate a variety of contributions and corrections to the electronic energy, such as infinite basis set extrapolation and core correlation effects. A full account of the procedure is given together with a rather large set of benchmark calculations on a set of 20 small molecules, from diatomics to tetratomics.

1. Introduction

The accurate calculation of vibrational spectra beyond the harmonic approximation is becoming increasingly feasible due the development of efficient computational methods for the purpose of and the increase in computational resources.

Beyond the harmonic oscillator (HO) model, a number of schemes are routinely used to calculate the molecular vibrational spectrum. One class of methods uses vibrational perturbation theory with the uncoupled harmonic oscillator as a zero-order description. Perturbation theory methods are very efficient when combined with a quartic force field description of the Born−Oppenheimer (BO) potential energy surface but are inherently not suited for medium or highly anharmonic systems. Another class of methods, which we will term explicit wave function methods to contrast them with the former, derives from a vibrational self-consistent field (VSCF)[1−3] calculation. In analogy with the Hartree−Fock method of electronic structure theory, a VSCF calculation affords a mean-field description of the multimode dynamics, and it represents an important starting point for more elaborate correlated calculations. In fact, mode−mode correlation is explicitly introduced by using a variety of methods, such as vibrational Møller−Plesset perturbation theory (VMP; by some, denoted as correlation-corrected VSCF, cc-VSCF),[4−9] vibrational configuration interaction (VCI),[2,3,10−15] vibrational coupled cluster (VCC),[13] and vibrational response theory.[16,17] The multiconfigurational time-dependent Hartree MCTDH approach[18] has been also used for calculation of vibrational spectra using internal coordinates.[19]

Despite being usually computationally more demanding than perturbative methods, wave-function-based methods are more general, more flexible and potentially more accurate,[20] and, in principle, capable of describing very anharmonic vibrational motions. A meaningful description of multimode correlation requires an accurate representation of the anharmonic part of the potential energy surface, usually, but not always, far from the equilibrium geometry. This means that a large portion of the BO hypersurface has to be calculated with electronic structure methods, and this represents one of the bottlenecks of every calculation of molecular vibrational dynamics. In fact, since the dimensionality of the hypersurface grows linearly with the number of atoms in the molecule, the number of vibrational modes is $3N - 6$ ($3N - 5$ for linear molecules) for a molecule with N atoms; the calculation of a fully coupled PES is prohibitive except for the smallest molecules.

One standard route to construct potential energy and property surfaces for use in vibrational structure calculations is based on the *n*-mode representation, where the full-dimensional PES is approximated as a sum of potential energy functions (PEFs) of lower dimensionality. Within this approach, high-order mode couplings are included in a hierarchical way. This hierarchy was originally suggested and implemented in the vibrational context by Carter and co-workers up to four mode couplings.[21] A similar approach restricted to two mode couplings was suggested and since then has been extensively used by Gerber and co-workers.[5,22] For rigid molecules, such mode-coupling expansions converge fast with the mode-coupling level, and often, the inclusion of up to three mode-coupling terms provides sufficiently accurate fundamental vibrations. Therefore, the mode-coupling approach is becoming a standard way for constructing accurate approximate PESs and has been generalized and extended in various ways and combined with various techniques for obtaining efficiency in the calculations.[5,14,23−29]

The PEFs included in the representation of the BO energy can be calculated on grids or represented as a low-order (typically of fourth order) Taylor expansion around the equilibrium geometry. Although computationally very attractive, the representation of the potential given by a low-order Taylor expansion is however not appropriate for the accurate description of the PES in regions far from the equilibrium geometry,[30] and the use of grid-based methods must be preferred. However, when each of the PEFs included in the expansion of the BO surface

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is represented in a grid, the number of single-point electronic structure calculations still increases significantly since the description of the n mode-coupling terms in a grid with G grid points per dimension for a system with M vibrational modes requires a number of evaluations of the order of $\binom{M}{n}G^n$.

Recently, we implemented an adaptive density-guided approach (ADGA) for accurate and flexible representation of the PEFs relevant to the quantum dynamics calculation.[31] The method is an extension of our previous static grid approach,[27] and it allows for a dynamical and automatic generation of the grid for each PEF included in the expansion of the fully coupled PES. The terms static and dynamic refer here to whether the grid settings are defined by user input (static) or whether they are determined iteratively. In the ADGA, the densities of the vibrational wave functions are used to guide the dynamic generation of the grids of evaluation points. Our tests confirmed that the algorithm is robust and efficient while optimizing the number of sampling points. It provides thus a consistent savings in the computational cost required for the construction of accurate PESs.

In this paper, we present a multiresolution adaptive density-guided approach (MADGA) that combines our iterative procedure with the multiresolution techniques to improve several aspect of the PES construction, namely, (a) higher-order coupling terms that are usually less important in the hierarchical representation of the potential but more expensive from the computational point of view can be included in approximate fashion by computing them with a less demanding method or adopting a smaller basis set; (b) a variety of contributions and corrections to the electronic energies can be easily included, for example, infinite basis set extrapolation, all-electron core correlation, and relativistic effects; and (c) a computationally less demanding method (e.g., density functional theory, DFT) is used to evaluate an educated guess for the position of the boundaries of the sampling grids. This improves the convergence rate when the actual sampling is carried out with a more accurate and time-consuming method (e.g., coupled cluster).

We note that the idea of resolving mode-coupling terms at different levels of theory is certainly not new in the field, and successful applications of the methodology have been presented by Rauhut et al.[32−35] and by Yagi et al.[26,29,36,37] However, the focus of these works was mostly put on the first of the aforementioned points, with the exception of ref 36. We also refer to ref 38 for an overview of the multiresolution concept.

With the potential offered by the multiresolution approach in concert with our recently developed ADGA for the automatic generation of the PES, we aim at developing some guidelines with respect to the use of its wide flexibility. We thus present a comparative survey of the theoretical methods to achieve an accurate but cost-efficient description of the BO PES to be used in anharmonic frequencies calculations.

The paper is organized as follows. In section 2, we describe the algorithm used for the generation of the grids of evaluation points, relating it to the previous works.[27,31] The computational details are presented in section 3, while results of the benchmark calculations are reported in section 4. Conclusions and perspectives are given in section 5.

2. Description of the Method

In this section, a brief introduction of the vibrational Hamiltonian and the potential energy operator is given. Furthermore, the implementation of the adaptive procedure for the construction of the PES is revised, and a detailed description of the multiresolution approach is reported.

2.1. The Vibrational Hamiltonian and the Potential Energy Operator. Vibrational energies and vibrational contributions to molecular properties are obtained from the solution of the BO vibrational Schrödinger equation. The Hamiltonian in mass-weighted rectilinear normal coordinates ($q_m \in \mathbf{Q}$) can be written as

$$H = T(\mathbf{Q}) + V(\mathbf{Q}) \tag{1}$$

where $T(\mathbf{Q})$ is the kinetic energy operator (either in the Watson form[39] or simply as a sum of $-\mathrm{d}^2/2\mathrm{d}q_m{}^2$ terms; for details and further references, we refer to our previous ref 27) and $V(\mathbf{Q})$ is the BO potential energy term.

In order to reduce the large dimensionality of the problem associated with the computation of the potential energy surface, the restricted mode-coupling representation of the fully coupled potential is adopted.[5,14,21,23,25] One starts by defining a set of potential energy functions (PEFs) which includes the coupling among a subset n of the M vibrational coordinates

$$\begin{aligned} V^{m_1} &= V(0, ..., 0, q_{m_1}, 0, ..., 0) \\ V^{m_1,m_2} &= V(0, ..., 0, q_{m_1}, 0, ...0, q_{m_2}, 0, ..., 0) \end{aligned} \tag{2}$$

and so forth up to $V^{m_1,m_2,...,m_M}$, the fully coupled potential, $V(\mathbf{Q})$. In eq 2, $m_i \neq m_j$. For the sake of simplicity, the set of modes (referred to as a mode combination, MC, hereafter) defining the particular PEF is collected in an n-dimensional vector $\mathbf{m}_n$, so that an n-dimensional PEF is denoted as $V^{\mathbf{m}_n}$. One further notes that by summing over all MCs, overcounting is introduced since each PEF includes all of the lower-dimensional PEFs corresponding to the set of $\mathbf{m}_{n'} \subset \mathbf{m}_n$. In order to avoid overcounting, potentials $\bar{V}^{\mathbf{m}_n}$ are conveniently introduced (see ref 25 for details), such that

$$V = \sum_{\mathbf{m}_n \in \mathrm{MCR}\{V\}} \bar{V}^{\mathbf{m}_n} \tag{3}$$

where MCR is a mode combination range, the set of MCs we want to include in the potential.

Extensive experience on medium size molecules tells us that a three- or four-mode coupling representation of the potential is usually sufficient for quantitative comparison with experiments, at least for the fundamental levels or low-lying overtones and combination bands of semi-rigid molecules.

2.2. The ADGA and the Analytical Representation of the Potential. In this work, we adopt the ADGA for the generation of the potential energy surfaces as described in ref 31. Very briefly, at a given mode combination level n, all $\binom{M}{n}$ n-dimensional PEFs, $V^{\mathbf{m}_n}$, are sampled in a set of grid points by means of ab initio electronic structure calculations. An analytic representation is then obtained by fitting each of the PEFs to a multivariate polynomial in frequency-scaled mass-weighted normal coordinates (for more details, we refer to ref 27). With this procedure, the vibrational Hamiltonian is expressed as a sum over T products of single-mode operators

$$\hat{H} = \sum_{t=1}^{T} c_t \prod_{m=1}^{M} \hat{h}^{m,t} \tag{4}$$

where c_t is the expansion coefficient and each term in the summation is a product of M one-mode operators, $h^{m,t}$, of the form q_m^n or a derivative $(\mathrm{d}/\mathrm{d}q_m)^n$ (with $n \geq 0$ and $q_m^0 = (\mathrm{d}/\mathrm{d}q_m)^0 = 1$). The computational advantages of Hamiltonians in the sum-over-products form, as in eq 4, are important and well-established in time-dependent quantum dynamics[18] and in vibrational structure theory.[40]

The ADGA merges the computational advantages of Hamiltonians of the form in eq 4 in vibrational structure theory,[40] with an adaptive determination of the sampling grids. In order to obtain a black box procedure for the determination of accurate PEFs, a few basic ideas were incorporated in the design of the algorithm, (i) the spatial extension of the vibrational wave function determines the boundaries of the sampling grids, (ii) the construction of each of the potential terms initiates with the calculation of the sampling points on a "minimal" grid, (iii) sampling points are iteratively added to the grids until convergence is achieved, and (iv) vibrational wave functions are used to construct vibrational densities (ρ), and those are used as key quantities in the construction of $\rho \times V$ "energy-like" contributions that help to identify the importance of each mode coupling as well as the optimized grid mesh for their descriptions.

2.2.1. The Vibrational Densities and the Determination of the Optimal Boundaries for the Monodimensional Grids. After a vibrational self-consistent calculation, the VSCF vibrational density for mode q_m, averaged over N^m modals, can be constructed as

$$\rho_{\mathrm{av}}(q_m) = \frac{\sum_{i^m}^{N^m} |\phi_{i^m}^m(q_m)|^2}{N^m} \tag{5}$$

In eq 5, $\phi_{i^m}^m(q_m)$ are the set of VSCF modals for mode m, and N^m is input by the user. The N^m values allow the user to construct an average density that specifically refers to the chemical problem under investigation (e.g., N^m should be at least equal to the number of vibrational states of interest). In this way, also higher excited states can be targeted during the construction of the PES by increasing N^m; see ref 31.

By construction, the VSCF average vibrational density integrates to 1 over the full configuration space, and this feature is used in the ADGA to ensure that the grid of points for the construction of the PES covers the configurational space explored by the vibrational wave functions. To be specific, if the integral values of the $\rho_{\mathrm{av}}(q_m)$ over the grid boundaries is smaller than 0.999, the grid is extended (see ref 31 for details). As the extension of the grid domains is iteratively adjusted in the ADGA to include the vibrational density, the procedure is usually started with relatively small grids centered on the reference geometry. A preoptimization of the boundaries for the monodimensional grids with an inexpensive method of calculation is implemented in the multiresolution formulation of the ADGA, vide infra.

2.2.2. Convergence of the Analytic Representation of the PES. Let us briefly consider how monodimensional grids are optimized in the ADGA. Every monodimensional grid is subdivided in subsectors, defined as the intervals between two adjacent sampling points. The nth iteration starts with the evaluation of the PEFs in correspondence to test points generated in the $(n - 1)$th iteration. In the first iteration, three energy evaluations are required, in correspondence of the left and right boundaries of the grid and the equilibrium geometry; those points define thus two subsectors. An analytical representation of the $V^{\mathbf{m},n\mathrm{th}}$ terms is then provided via a polynomial fitting (superscript nth refers to the nth iteration). The potential is then used in a VSCF calculation for the ground vibrational state, and the VSCF modals are then used to construct the vibrational density $\rho_{\mathrm{av}}^{n\mathrm{th}}$ for mode q_m. For each subsector, we can define an "energy-like" contribution, $(\rho V)_i^{n\mathrm{th}} = \int_i \rho_{\mathrm{av}}^{n\mathrm{th}}(q_m) V^{\mathbf{m},n\mathrm{th}}(q_m)\mathrm{d}q_m$. A further testing point is added at the middle point of the subsectors for which the condition

$$\frac{(\rho V)_i^{n\mathrm{th}} - (\rho V)_i^{(n-1)\mathrm{th}}}{(\rho V)_i^{n\mathrm{th}}} < \varepsilon_{\mathrm{rel}} \tag{6}$$

is not fulfilled. Here, $(\rho V)_i^{(n-1)\mathrm{th}}$ is taken equal to 0 at the first iteration. In other words, an interval where the relative variation of the integral value $(\rho V)_i$ between two iterations is found to be larger than a specified threshold (usually on the order of 1.0%) is further subdivided with the addition of a new testing point. Furthermore, intervals with a small contribution to the energy are not further subdivided, regardless of the relative error computed by means of eq 6. In particular, a subsector is not further divided if the condition

$$(\rho V)_i^{n\mathrm{th}} - (\rho V)_i^{(n-1)\mathrm{th}} < \varepsilon_{\mathrm{abs}} \wedge (\rho V)_i^{n\mathrm{th}} < \varepsilon_{\mathrm{abs}} \tag{7}$$

is fulfilled, with $\varepsilon_{\mathrm{abs}}$ being usually on the order of 10^{-6} au. The nth iteration ends with the definition of the new subsectors and the calculation and storage of the integrals to be used in the subsequent iteration.

The ADGA converges hierarchically up to a user-specified maximum mode combination level, that is, monodimensional PEFs are converged before the bidimensional and so on. The adaptive construction of the n-dimensional grids is a straightforward generalization of the procedure outlined above;[41] the multidimensional grid domains are partitioned in subsectors defined by 2^n adjacent points (see Figure 2 in ref 31 for a graphical representation), the convergence criteria are n-dimensional generalizations of the criteria outlined above, and the n-mode densities for the construction of the $(\rho V)_i$ quantities are taken to be a direct product of the converged one-mode densities ($\rho(q_m)$) as

$$\rho(q_{m_1}, q_{m_2}, ..., q_{m_n}) = \prod_{i=1}^{n} \rho(q_{m_i}) \tag{8}$$

2.3. The Multiresolution Implementation. In a multiresolution procedure for PES construction, PEFs computed with different methods and/or approximations (electronic structure methods, basis sets, analytic representations, and electronic structure codes) are combined to obtain a hybrid PES.[26,32−34,36] In particular, we refer to ref 26 for an exhaustive discussion of the multiresolution formalism adapted to the intrinsic mode-coupling framework.

In the multiresolution implementation, the ADGA is used for the construction of the various PEFs entering in the final PES. In the multiresolution construction of PESs, not just the electronic structure methods and basis sets but also the electronic structure program can vary between the different levels. Our current implementation in MidasCpp[42] includes interfaces to GAMESS,[43] Dalton,[44] and ACESII.[45]

Since it was observed that accurate determination of the initial conditions for the boundaries of the monodimensional grids may improve the convergence rate both with respect to number of evaluation points and ADGA iterations,[31] in the construction of the PEFs for the *i*th level, the optimized boundaries for the monodimensional grids of the ($i-1$)th level are used, and four instead of two evaluation points are requested for each mode in the first iteration. Formally, this allows for a preoptimization of the grid boundaries, and the use of an educated guess for the position of the grid boundaries was found to reduce consistently the computational efforts for the convergence of the monodimensional PEFs.

The analytic representation of the PESs is obtained, as described above, via a multidimensional linear least- squares fitting realized in a direct product polynomial basis using frequency-scaled mass-weighted normal coordinates. As the polynomial basis for the fitting is uniquely defined during the MADGA, the PESs obtained at each level may be easily combined by manipulating the coefficients of the polynomial expansion with a linear combination formula. Under the name of linear combination recipes, it is possible to define two major types of combinations of PESs to give rise to hybrid PESs; (i) PESs that share the same maximum mode combination level can be combined to include a extrapolation procedure (vide infra) and/or linear corrections, and (ii) PESs with a low maximum mode combination level can be corrected by adding higher mode combination terms from PESs constructed with computationally less expensive electronic structure methods. Both of these functionalities have been implemented, and as an example, it is possible to obtain in an automatic and black box fashion a hybrid PES where the one-mode coupling terms are computed at the coupled cluster level with an infinite basis set extrapolation, the two-mode couplings terms are computed at the MP2 level, and the three-mode terms are computed with DFT.

The availability of an analytic form of the PESs enable us to construct in a straightforward manner a hybrid PES as a linear combination of the PES with a common maximum mode combination level. The reason behind this kind of operation relies on the observation that a variety of effects such as all-electron core correlation, relativistic effects, as well as infinite basis set extrapolation can be included in the electronic energy by means of linear combinations.

As an example, we report the procedure to obtain hybrid PESs incorporating infinite basis set extrapolation of the electronic energy and all-electron core correlation corrections. Under the assumption that the SCF reference energy converges faster than the correlation energy with respect to the cardinal number of the basis set, we limited the extrapolation procedure to the correlation energy using the two-points scheme of Halkier et al.[46]

$$E_{\infty}^{\mathrm{corr}} \approx E_{XY}^{\mathrm{corr}} = \frac{E_X^{\mathrm{corr}} X^3 - E_Y^{\mathrm{corr}} Y^3}{X^3 - Y^3} \qquad (9)$$

where X and Y are the cardinal numbers of the basis set used in the extrapolation. Assuming that the reference energy is converged at the basis set with the larger cardinal number Y, the extrapolated energy can be written as $E_{XY} = E_Y^{\mathrm{SCF}} + E_{XY}^{\mathrm{corr}}$. With the total energy computed at the CCSD(T) level, the extrapolated energy can be written as

$$E_{XY} = E_Y^{\mathrm{SCF}} + \frac{(E_X^{\mathrm{CCSD(T)}} - E_X^{\mathrm{SCF}})X^3 - (E_Y^{\mathrm{CCSD(T)}} - E_Y^{\mathrm{SCF}})Y^3}{X^3 - Y^3} \qquad (10)$$

In practice, the expansion coefficients of the analytic form of four PESs ($\mathrm{PES}_X^{\mathrm{CCSD(T)}}$, $\mathrm{PES}_Y^{\mathrm{CCSD(T)}}$, $\mathrm{PES}_X^{\mathrm{SCF}}$, and $\mathrm{PES}_Y^{\mathrm{SCF}}$) are combined according to eq 10 to obtain the extrapolated potential energy surface (PES_{XY}).[47]

Furthermore, with the availability of the MP2 calculations within the frozen core and the all-electron approximation, it is possible to devise a correction for the core correlation at the MP2 level (cc_X) by considering the difference

$$\mathrm{cc}_X = E_{\text{ae-MP2/aug-cc-pCVXZ}} - E_{\text{fc-MP2/aug-cc-pVXZ}} \qquad (11)$$

where the ae-MP2 represents a MP2 calculation with all-electron calculation (aug-cc-pCVXZ basis set) and fc-MP2 is the frozen core version with the corresponding aug-cc-pVXZ. As for the extrapolation procedure, the core correlation correction formula for the single-point energy calculation can be directly used with the analytic forms on the PES.

3. Computational Details

We tested the MADGA on a set of 20 molecules, divided into subsets according to the number of atoms. We considered seven diatomic molecules, namely, CO, HF, N_2, Cl_2, F_2, CS, and HCl, whereas Cl_2O, HOF, H_2S, SO_2, HCN, HOCl, OCS, CO_2, CS_2, and HNO were considered as representatives of the triatomic molecules. It should be noted that the last three molecules are linear, and therefore, they have four normal modes. The tetratomic molecules investigated are F_2CO, H_2CO, and Cl_2CO.

The construction of PESs requires an input of vibrational frequencies and normal coordinates. For the diatomic molecules, this a trivial as there is obviously only one coordinate. Rather arbitrarily, the minimum and thus the normal coordinates were computed by means of DFT calculations as implemented in the DALTON quantum chemistry program[44] and using the CAM-B3LYP exchange−correlation potential[48] in combination with the cc-pVDZ.[49,50] For the other molecules, the normal coordinates were computed at the coupled cluster level of theory using the coupled cluster singles and doubles (CCSD) parametrization and the correlation-consistent polarized valence double-ζ basis set (cc-pVDZ)[49,50] as implemented in the ACESII suite of programs.[45] These levels are far from optimal in the sense of producing highly accurate structures; however, a key component of our approach is that the identification of the exact minimum should not be crucial as the adaptive procedure should steer the position of the evaluation points anyway. The possibility of using lower-quality normal coordinates compared to the quality of important single-point evaluation points for the anharmonic calculation has been investigated and confirmed before without an adaptive algorithm.[51] Since this may well be convenient in many applications, we will also test this here.

For each of the molecules under examination, a series of PESs has been constructed with different electronic structure methods and basis sets. Concerning the ab initio methods, coupled cluster singles and doubles with perturbative triples correction CCSD(T) (hereafter, the notation CC will refer to CCSD(T), except where differently stated) and Møller−Plesset second-order perturbation theory (MP2) were combined with augmented correlation-consistent polarized valence basis sets of double- through quadruple-ζ quality aug-cc-pVXZ, X = D, T, and Q[49,50,52] (hereafter, DZ, TZ, QZ). Besides the standard calculations, where the correlation treatment was limited to the valence electrons (frozen core approximation, fc), a second set of MP2 calculations for all of the molecules and CCSD(T) calculations for the diatomic molecules were carried out with all electrons (ae) correlated. For these calculations, the augmented correlation-consistent polarized core−valence basis sets of double- through quadruple-ζ quality (aug-cc-pCVXZ, X = D, T, Q)[49,50,52−55] were used.

As described in the previous section, PESs constructed with basis sets of increasing quality can be combined to obtain a PES where the infinite basis set limit is approached. In the remainder of the article, we will use Extr.*XY* to refer to the basis set extrapolation procedure involving the *XZ* and *YZ* basis sets of eq 10, whereas the notation cc_X will be used when referring to the MP2 core correlation correction of eq 11 computed with an *XZ* quality basis set.

A number of exchange−correlation (xc) functionals/basis set combinations were investigated within density functional theory. In the attempt to cover a representative set of the more accurate functionals available, we included in the survey the following xc functionals: pure DFT generalized-gradient approximations (GGA) functionals such as BP86[56,57] and OLYP,[58,59] hybrid GGA functionals such as PBE0,[60,61] and the long-range corrected Coulomb attenuated CAM-B3LYP[48] as well as meta-GGA functionals, both pure M06-L and hybrid M06.[62] Combined with these functionals, a series of basis set were tested, double-ζ Dunning basis sets[63,64] improved with a polarization function (DuDZP), the triple-ζ Dunning[65] (DuTZ), Pople split valence double-ζ with polarized and diffuse functions[66−69] (6-31G+*), and the polarization consistent basis set from Jensen[70−73] (PC1 and PC2) together with their versions augmented with a set of diffuse functions (APC1 and APC2).

Since a complete survey using all of the aforementioned methods/basis set combinations is out of reach for the entire pool of molecular systems investigated in the paper, a hierarchical approach was adopted. The results obtained in the study of the diatomic systems is used to select a smaller but yet more efficient set of methods/basis combinations for the triatomic molecules. In the same manner, the methods used for the larger molecules are selected in an attempt to optimize the accuracy and the cost of the construction of the PES based on the information obtained with the smaller molecules. Furthermore, starting with the triatomic molecules, the accuracy and reliability of hybrid PESs where mode-coupling terms are resolved at different levels of theory are tested.

For simplicity, we decided from the outset to use only the simplified kinetic energy operator for all PESs of all molecules as the focus was on the PES construction. The effect of using the complete Watsonian versus the simplified kinetic energy operator was subsequently tested for all states of all molecules. Whereas for three molecules, H_2CO, H_2S, and HCN, the coriolis contributions were found to be quite significant for specific fundamental excitations (with maximum effects of up to 13.6, 6.3, and 6.8 cm^{-1}, respectively, in agreement with the results of Carbonniere and Barone[74]), for the remaining systems, the effect was found to be small (on the order of 1 cm^{-1} for the fundamentals). The effects were found not to alter effect the statistical analysis and conclusions on the PES part significantly. For high accuracy relative to experiments, especially for some vibrations involving the light H atoms, incorporation of the effects due to the extra terms in the Watsonian is recommended.

The one-mode vibrational densities used in the ADGA are obtained after VSCF calculations on the ground vibrational states. Since a VSCF wave function is exact for a system with a single mode of vibration, VSCF calculations have been performed in the monodimensional test cases. For the larger molecules, we use the VCI method for the final results; a full-VCI (FVCI) parametrization is selected for the three-atomic molecules, whereas a VCI[gs,4] parametrization for the vibrational wave function is used for systems with more than three vibrational coordinates. In all cases, the lowest eight VSCF modals per mode are retained in the VCI calculations. The VSCF modals are expanded in a set of distributed Gaussians, generated from a density of Gaussian equal to 0.8; the details for this basis set can be found in ref 31. Preliminary convergence tests demonstrate that the VSCF results are converged with respect to the basis set. The maximum polynomial degree used for the fitting of the monodimensional and multidimensional surfaces is 12. In the early cycles of the iterative procedure, few evaluation points are available, and the maximum degrees of the fitting polynomials are reduced to $n - 1$, with n being the number of evaluation points.

Concerning the thresholds used in the ADGA procedure (see ref 31 for details), the monodimensional surfaces were converged with $\varepsilon_{rel} = 5 \times 10^{-3}$ and $\varepsilon_{abs} = 5 \times 10^{-7}$, the bidimensional surfaces were converged with $\varepsilon_{rel} = 5 \times 10^{-2}$ and $\varepsilon_{abs} = 5 \times 10^{-6}$, and the three-dimensional surfaces were converged with $\varepsilon_{rel} = 2 \times 10^{-1}$ and $\varepsilon_{abs} = 2 \times 10^{-5}$. These convergence thresholds ensure that the representation of the PEFs were tightly converged. Whereas the analysis of the efficiency of ADGA in terms of single-point calculations necessary for the construction of the PES resides beyond the scope of this article, we report, as an example of the performances achieved with the adaptive procedure, that the 3M-PES obtained at the DFT level for F_2CO required 1174 single-point calculations (712 taking into account molecular symmetry).

The boundaries of the monodimensional grids were iteratively determined by requiring that 99.9% of the mean density constructed from the four lowest vibrational states for each vibrational mode was included in the boundaries of the monodimensional grid ($N^m = 4$ in eq 5). Exploratory tests confirmed that the choice of constructing the mean density including the four lowest vibrational states provides well-converged fundamental and first overtone excitation energies. With a larger value of N^m, the outcome potentials will be suitable for the calculation of even higher vibrational states but at a higher computational cost as a larger space has to be explored.

These boundaries were preoptimized by using the ADGA and CamB3LYP/DuDZP with the aforementioned thresholds and parameters. The initial boundaries were, in turn, specified to correspond to the harmonic classical turning points for $v = 1$.

4. Results

4.1. Diatomic Molecules. Table 1 reports the fundamental and first overtone excitation energies for carbon monoxide, CO, as a function of electronic structure methods and basis sets used for the construction of the PES. For the sake of simplicity, only selected combinations have been included in the paper, and the reader is referred to the Supporting Information for a more complete overview. For the diatomic molecules considered in this work, the reference values were computed using the power series for the vibrational energy

$$G = \omega_e(\nu + 1/2) - \omega_e\chi_e(\nu + 1/2)^2 + ...$$

TABLE 1: Fundamental and First Overtone Vibrational Frequencies of CO[a]

	Frozen Core								Frozen Core + Core Correlation
exp.	CC/QZ	CC/TZ	CC/DZ	MP2/QZ	MP2/TZ	HF/QZ	CC/Extr.TQ	CC/Extr.DT	CC/Extr.TQ+cc$_Q$
2143.3	−9.3	−24.8	−64.9	−46.9	−59.8	260.4	−1.8	−17.5	8.2
4259.9	−18.1	−49.0	−129.2	−93.5	−119.2	524.9	−3.3	−34.4	16.7
MAD	13.7	36.9	97.1	70.2	89.5	392.7	2.6	26.0	12.5

	All Electron							
exp.	CC/QZ	CC/TZ	CC/DZ	MP2/QZ	MP2/TZ	HF/QZ	CC/Extr.TQ	CC/Extr.DT
2143.3	0.3	−15.9	−61.2	−36.6	−53.8	260.7	8.3	−7.5
4259.9	0.9	−31.2	−121.9	−73.1	−109.5	525.6	16.9	−14.6
MAD	0.6	23.6	91.6	54.9	81.7	393.2	12.6	11.1

[a] Relative to the experimental values, in cm^{-1}. Mean absolute deviations (MAD) are reported. CC stands for a CCSD(T) calculation.

truncated at the second term. The coefficients ω_e and $\omega_e\chi_e$ were taken from ref 75.

Inspection of the data presented in Table 1 allows for some preliminary remarks; for each of the PESs, the discrepancy observed for the first overtone with respect to the experimental result is roughly twice the error observed for the fundamental frequency. The use of correlated electronic structure methods is mandatory to achieve good accuracy for the vibrational energies. In fact, potentials calculated at the HF level are of low quality, and consequently, the experimental vibrational energies are poorly reproduced. Moreover, an adequate basis set has to be chosen, as indicated from the increase in accuracy when going from a double to a quadruple-ζ quality basis set. Comparison of the "frozen core" and "all electron" results in the table reveals that the core correlation effects account for about 4−10 cm^{-1} of the fundamental frequency, depending on the model/basis set combination. Furthermore, the performances of the basis set extrapolation procedures are investigated in Table 1; taking as an example the "frozen core" section, the errors on the fundamental frequencies obtained at double-, triple-, and quadruple-ζ quality basis set are −64.9, −24.8, and −9.3 cm^{-1}, respectively, whereas the error of the extrapolation procedure involving double- and triple-ζ quality basis sets, CC/Extr.DT, is −17.5 cm^{-1}, and that corresponding to the extrapolation procedure involving triple- and quadruple-ζ quality basis sets, CC/Extr.TQ, is −1.8 cm^{-1}. Clearly, the use of the extrapolation improves the result obtained with a finite basis set toward the infinite basis set limit. Also, it is clear from the inspection of the "all-electron" section in Table 1 that the extrapolated values follow the trend given by the parental data; the errors in the fundamental frequency are −61.2, −15.9, and 0.3 cm^{-1}, respectively, with double-, triple- and quadruple-ζ quality basis sets, while the CC/Extr.DT value is −7.5, and the Extr.TQ is 8.3 cm^{-1}. When the core correlation correction computed at the MP2 level is added, the values match the all-electron CC/Extr.TQ results. Whereas this confirms that the core correlation correction computed at MP2 give sensible values, it also proves that our best ab initio settings may give less accurate results than a less sophisticated approach. In fact, some results in Table 1 may be puzzling at first glance; the all-electron CC/Extr.TQ results are less accurate that those obtained with a quadruple-ζ quality basis set, and the second best result is obtained with the CC/Extr.TQ basis in the frozen core approximation.

The unexpectedly accurate performances for some combinations, as seen for CO in Table 1, are due to a consistent cancellation of errors. In fact, Ruden et al. investigated the impact of connected high-order excitations, core correlation, and basis sets on the fundamental frequencies of diatomics calculated with coupled cluster,[76] concluding that the use of a finite basis set as well as the neglect of core correlation introduces a negative error on the calculated frequencies; on the other side, the discard of excitation levels in the coupled cluster model introduces a positive error. Recently, Werner and co-workers addressed the same issues for the calculation of anharmonic vibrational frequencies for molecules with up to six atoms, and they were able to conclude that in the absence of heavy atoms, the errors due to high-order electron correlation and core correlation effects conveniently cancel, and the calculated property may be degraded if only one of the effects is accounted for.[77]

Table 1 is useful to introduce the procedure followed in the survey on the diatomic systems. In Table 2, we report for the fundamental frequency of every molecule the absolute deviation (AD) of the calculated results from the experimental values. Moreover, the accuracy of the set of data for each electronic structure method/basis set is measured with an average value where the largest and smallest contributions are neglected to provide a single accuracy index which is less sensitive to outliers. Concerning the frozen core approximation, the truncated mean of the AD shows that, as observed before, the accuracy is increased with the use of larger basis sets and the basis set extrapolation procedure. In particular, the accuracy of the results follows the following trend: DZ < TZ < Extr.DT < QZ < Extr.TQ as the accuracy indexes are found to be 53.1, 12.5, 8.2, 5.5, and 4.5 cm^{-1}, respectively. Whereas the truncated mean of the AD provides an accurate estimation of the performances of a given electronic structure model/basis set combination, the information of the direction of the errors is lost. Nevertheless, the analysis of the raw data confirms the trends already observed; when core correlation effects and complete basis sets are simultaneously accounted for, the fundamental frequencies are overestimated due to the neglect of high-order electron correlation. The error cancellation gives rise to some subtle variation in the results, showing that the inclusion of higher excitation is necessary for full control over the last few cm^{-1}. Nevertheless, the accuracy obtained with the large basis sets and the extrapolated surface is quite satisfactory. On the other hand, the values obtained with CCSD(T) together with a double-ζ basis set are, on average, about 45 cm^{-1} apart from the reference values.

An average error of 50 cm^{-1} is observed when using MP2 and a relatively large basis set. Due to the size of the errors observed, the number of electrons correlated (fc versus ae) and the quality of the basis set (TZ versus QZ) are found to have little effect on the accuracy of the PES. Despite their inaccuracy, sensible corrections for the core correlation effects can be devised, as demonstrated by the fair agreement between the all-electron calculation and the corresponding frozen core with MP2

TABLE 2: Absolute Deviation from the Experimental Values of the Calculated Fundamental Vibrational Frequencies of the Diatomic Molecules As a Function of the Method/Basis Set Combination[a]

	Frozen Core							Frozen Core + Core Correlation					
	Extr.TQ	QZ	TZ	Extr.DT	DZ	MP2/QZ	MP2/TZ	Extr.TQ+cc_Q	Extr.TQ+cc_T	Extr.DT+cc_Q	Extr.DT+cc_T	QZ+cc_Q	TZ+cc_T
CO	1.8	9.3	24.8	17.5	64.9	46.8	59.8	8.2	7.6	7.6	8.2	0.7	15.5
HF	14.2	6.7	6.8	4.8	67.6	6.8	3.9	16.5	13.6	6.9	4.0	8.9	7.6
N_2	5.4	3.3	18.3	8.5	39.9	166.3	181.4	15.8	18.1	2.0	4.3	7.2	5.6
Cl_2	0.9	6.2	17.7	12.7	57.6	22.7	14.6	6.7	7.2	7.3	6.8	0.6	11.8
F_2	11.7	4.0	2.2	4.1	92.5	92.4	91.4	12.9	13.8	5.3	6.2	5.3	0.1
CS	2.2	7.1	17.6	10.8	35.6	20.2	13.1	9.4	8.7	0.8	0.2	4.5	6.7
HCl	1.3	0.1	1.1	2.9	20.7	57.9	59.1	10.3	10.7	14.7	15.1	11.8	11.1
mean	4.5	5.5	12.5	8.2	53.1	48.0	47.6	11.3	10.9	5.8	5.9	5.3	8.6

	All Electron						
	Extr.TQ	QZ	TZ	Extr.DT	DZ	MP2/QZ	MP2/TZ
CO	8.3	0.3	15.9	7.5	61.2	36.6	53.8
HF	17.6	9.0	8.0	2.9	66.2	9.0	4.7
N_2	13.5	6.1	6.6	5.6	36.1	153.1	165.4
Cl_2	6.6	0.8	11.8	6.1	54.0	27.7	19.7
F_2	12.2	4.8	0.7	5.1	89.3	93.1	92.9
CS	8.3	3.0	7.7	0.0	30.5	30.9	23.1
HCl	9.7	11.1	10.5	13.6	11.2	69.1	70.7
mean	8.5	2.9	6.8	3.9	43.5	51.5	52.0

[a] The values are reported in cm^{-1}. If not differently stated, the method is CCSD(T). The truncated mean (the largest and smallest entries are discarded) is reported.

TABLE 3: PES Constructed with PBE0 with the Absolute Deviation from the Experimental Values of the Calculated Fundamental Vibrational Frequencies of the Diatomic Molecules As Function of the Basis Set[a]

	PBE0							
	DuDZP	DuTZ	TZ	631+G*	PC1	PC2	APC1	APC2
CO	55.0	81.2	66.7	68.2	78.8	69.6	75.4	69.0
HF	19.1	253.8	16.3	109.4	9.6	19.2	18.8	17.4
N_2	93.5	27.7	124.0	139.0	137.8	124.2	137.3	126.2
Cl_2	24.8	58.9	19.8	7.8	1.0	21.3	1.8	23.5
F_2	198.0	121.4	194.3	174.9	153.6	190.0	159.5	192.2
CS	38.5	97.9	48.3	43.3	43.9	47.5	45.0	47.1
HCl	13.0	254.5	15.8	0.2	8.4	11.9	3.7	11.3
mean	46.2	122.6	55.0	73.6	55.7	56.3	56.0	56.7

[a] The values are reported in cm^{-1}. The truncated mean (the largest and smallest entries are discarded) is reported.

TABLE 4: Summary of the Performances for Each Functional/Basis Combination on the Set of Diatomic Molecules[a]

	DuDZP	DuTZ	TZ	631+G*	PC1	PC2	APC1	APC2
BP86	92.9	203.8	59.6	75.4	65.9	60.7	65.2	60.3
PBE0	46.2	122.6	55.0	73.6	55.7	56.3	56.0	56.7
OLYP	69.1	190.2	43.8	52.7	43.2	44.1	42.9	43.2
M06	40.5	106.7	60.7	50.4	52.9	63.1	54.4	61.3
M06-L	23.7	132.0	29.4	37.4	27.4	35.0	27.8	33.0
CamB3LYP	54.0	49.9	65.8	94.5	75.6	66.6	78.9	68.5

[a] As a truncated mean of the absolute deviation of the calculated fundamental frequencies with respect to the experimental values. The values are reported in cm^{-1}.

corrections (compare fc-CC/QZ+cc_Q versus ae-CC/QZ and fc-CC/TZ+cc_T versus ae-CC/TZ). Furthermore, it is interesting to note that the MP2 core correlation correction is quite independent of whether a TZ or QZ correction is used (fc-CC/Extr.TQ+cc_Q and fc-CC/Extr.TQ+cc_T versus ae-CC/Extr.TQ or fc-CC/Extr.DT+cc_Q and fc-CC/Extr.DT+cc_T versus ae-CC/Extr.DT). While the core correlation correction was not particularly useful for the diatomics, we shall return to it for the polyatomics.

The set of diatomic molecules was furthermore investigated by means of density functional theory, and the performance of 48 combinations (6 xc functionals and 8 different basis set) was studied. Table 3 reports the results obtained with the PBE0 functional; the AD for each of the molecules depending on the basis set adopted is shown together with the truncated mean for each basis set. The performance of each combination of xc functional/basis set is summarized in Table 4, and the analysis of the results clearly shows that the accuracy of the frequencies obtained with DFT is far from homogeneous. Despite the large variations in the results, some rules of thumb may be evinced; the presence of polarization functions is fundamental to achieve reasonable accuracy, as is evident from the rather inaccurate results obtained with the DuTZ basis set. The best performances are obtained with the aug-cc-pVTZ and with Jensen's (A)PC[1-2] basis sets. Considering the computational efficiency (a polarization consistent basis has fewer functions than the analogous correlation consistent basis), the (A)PC[1-2] basis set is preferred. The BP86 and CamB3LYP functionals are found to give the less accurate PESs; on the other hand, a quite satisfactory accuracy is achieved with the meta-GGA functionals and, in particular, with M06-L. The accuracy of the PES obtained with M06-L appears to be competitive with the one corresponding to any MP2 calculation or CCSD(T)/DZ. The set of calculations here preformed provides a first screening in the determination of a useful and accurate functional/basis set combination.

4.2. Triatomic Molecules.

The experimental reference values for the vibrational frequencies of the triatomic molecules are taken from the Computational Chemistry Comparison and Benchmark Database[78] (CCCBDB), maintained by the National Institute of Standards and Technology, with the exception of the values for HOF, which were taken form refs 79 and 80.

With the information collected for the diatomic systems, a strategy to tackle the triatomic systems was designed; it was decided to limit the coupled cluster calculations up to the triple-ζ quality basis set, and the core correlation correction was computed with triple-ζ, whereas the DFT calculations involved only four functionals (OLYP, PBE0, M06-L, and CamB3LYP) and three different basis sets (PC1, APC2 and TZ). The PES

TABLE 5: VCI[gs,4] Fundamental Frequencies of HCN Computed with PESs Constructed with a Selected Set of Ab Initio Methods and Basis Sets[a]

exp.	CC/Extr.DT+cc$_T$	CC/Extr.DT	CC/TZ	CC/DZ	ae-MP2/TZ	fc-MP2/TZ	harmonic[b]
712.0 (E)	−4.3	−5.9	−6.8	−31.4	3.9	2.8	30.3
2089.0 (A)	10.6	−0.4	−10.1	−41.9	−85.8	−98.4	86.1
3312.0 (A)	−7.0	−8.6	−17.8	−39.7	21.1	19.3	159.8
MAD[c]	6.5	5.2	10.4	36.1	28.7	30.8	76.7

[a] The values are reported in cm^{-1} relative to the experimental values. The symmetry of the mode is given in parentheses. CC stands for a CCSD(T) calculation. [b] At the CCSD/DZ level of theory. [c] The degeneracy of the modes has been accounted for in the calculation of the MAD.

TABLE 6: Potential Energy Surfaces Constructed with Ab Initio Methods and a Summary of the MAD Computed on the Fundamental Frequencies of the Triatomic Molecules[a]

	CC/Extr.DT+cc$_T$	CC/Extr.DT	CC/TZ	CC/DZ	ae-MP2/TZ	fc-MP2/TZ	harmonic[b]
CO_2	6.1	9.6	13.0	29.8	14.7	15.4	56.2
HOF	1.9	2.2	8.9	50.3	30.8	28.9	145.6
H_2S	5.2	8.9	11.7	29.0	48.6	42.9	94.2
SO_2	5.8	28.0	31.9	111.0	34.4	55.5	46.5
HCN	6.5	5.2	10.4	36.1	28.7	30.8	76.7
HOCl	3.7	5.9	11.1	39.7	17.9	18.3	115.5
OCS	2.3	4.6	8.4	24.8	7.7	5.2	34.0
CS_2	4.6	2.4	8.2	28.3	21.0	17.0	23.5
Cl_2O	3.3	2.5	6.2	27.8	17.9	13.9	39.8
HNO	5.9	8.5	10.4	36.2	57.9	60.8	166.1
mean	4.6	6.0	10.3	34.6	26.7	27.8	76.1

[a] The values are given in cm^{-1}. The truncated mean (largest and smallest values discarded) is reported for each of the method/basis combination. [b] At the CCSD/DZ level of theory.

for the triatomic molecules was constructed to include up to three mode couplings; this means that the fully coupled PESs were calculated for the nonlinear systems Cl_2O, HOF, H_2S, SO_2, HCN, HNO, and HOCl. The full-VCI parametrization was adopted in the vibrational calculations, (VCI[3] for the nonlinear molecules and VCI[4] for HCN, OCS, CO_2, and CS_2). Furthermore, the decision was made to address only the fundamental vibrational excitations in the vibrational calculations.

Table 5 shows the fundamental vibrational frequencies of HCN for various ab initio electronic structure methods used in the calculations of the molecular PES. To characterize the quality of each set of fundamental frequencies, the mean absolute deviation (MAD) from the experimental values has been calculated and included in the table. For comparison, the harmonic vibrational frequency computed at the CCSD level with a DZ basis is shown, and as expected from the particularly poor basis set, the errors are found to be particularly large. The results obtained at the CCSD(T) level with increasingly larger basis sets meet the expectation; the worst results are obtained when using the double-ζ basis (MAD = 36.1 cm^{-1}), a consistent improvement is observed with the triple-ζ basis (MAD = 10.4 cm^{-1}), while the basis set extrapolation reduces the MAD to 5.2 cm^{-1}. In this particular case, the inclusion of core correlation corrections provides a minor effect on the overall quality of the PES, and a slight increase in the average error is observed.

A summary of the data obtained with ab initio methods is given in Table 6, where the MAD for each molecule is reported as a function of the level of theory and the basis sets. The individual values are further combined into a truncated mean (the largest and smallest values are discarded) to provide a single index for the accuracy of the PESs. The overall picture confirms that, among the methods investigated, the PESs with the lowest accuracy are obtained with the CC/DZ chemistry model (34.6 cm^{-1}) followed by the MP2/TZ combinations (both in the frozen core and all-electron versions). The CC/TZ is found to be fairly accurate as the truncated mean is 10.3 cm^{-1}. A further improvement is obtained by using the basis set extrapolation technique, and the index for CC/Extr.DT is found to be 6.0 cm^{-1}.

TABLE 7: Potential Energy Surfaces Computed at the DFT Level and a Summary of the MAD Computed on the Fundamental Frequencies of the Triatomic Molecules[a]

	OLYP			M06-L			PBE0			CamB3LYP		
	PC1	APC2	TZ	PC1	APC2	TZ	PC1	APC2	TZ	PC1	APC2	TZ
CO_2	34.2	34.6	34.4	57.3	56.0	30.8	56.5	57.6	29.8	57.0	56.3	53.9
HOF	61.6	50.9	52.2	16.8	20.2	23.4	42.3	68.1	66.6	41.5	59.0	57.3
H_2S	49.4	49.3	47.5	18.8	21.4	17.8	13.2	12.9	13.7	12.6	11.3	11.4
SO_2	84.6	47.9	39.1	32.3	5.5	17.4	14.1	24.9	33.5	13.1	35.8	23.6
HCN	19.9	20.0	23.1	34.2	45.1	48.2	53.3	49.3	50.5	64.6	61.3	59.1
HOCl	75.9	39.5	41.3	24.1	11.2	11.8	12.1	34.3	32.0	15.5	29.6	26.3
OCS	16.1	12.7	11.8	24.6	29.1	29.8	22.9	28.4	28.8	23.7	28.9	25.8
CS_2	11.8	6.3	13.8	16.4	23.6	21.4	15.0	20.0	22.5	15.5	22.1	18.2
Cl_2O	70.3	43.6	45.9	51.3	34.3	34.2	14.4	28.7	26.8	12.4	37.6	35.7
HNO	118.3	96.3	97.2	83.0	93.1	93.7	73.4	56.5	56.7	61.1	68.9	66.6
mean	51.5	37.3	37.1	32.4	30.1	27.9	29.0	37.5	35.1	30.0	41.3	37.5

[a] The values are given in cm^{-1}. The truncated mean (largest and smallest values discarded) is reported for each of the functional/basis combination.

TABLE 8: VCI[gs,4] Fundamental Frequencies of HCN Computed with PESs Constructed with a Selected Set of Ab Initio Methods and Basis Sets[a]

		Pure PES			Hybrid PES						
					2D-PES		3D-PES				
	1D	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T
	2D	–	Extr.DT+cc_T	Extr.DT+cc_T	MP2/TZ	M06-L/APC2	Extr.DT+cc_T	Extr.DT+cc_T	MP2/TZ	MP2/TZ	M06-L/APC2
Exp.	3D	–	–	Extr.DT+cc_T	–	–	MP2/TZ	M06-L/APC2	MP2/TZ	M06-L/APC2	M06-L/APC2
712.0		123.1	−90.8	−4.3	−111.4	−70.6	−3.6	−5.6	−8.9	−11.0	−2.5
2089.0		20.5	7.7	10.6	0.1	39.2	11.9	10.7	11.5	10.3	13.1
3312.0		56.8	−5.5	−7.0	−8.8	11.0	−6.6	−7.2	−4.0	−4.6	−3.0
MAD		80.9	48.7	6.5	57.9	47.8	6.4	7.3	8.3	9.2	5.3

[a] The values are given in cm^{-1} relative to the experimental values. If not stated differently, the method used is CCSD(T).

TABLE 9: Hybrid Potential Energy Surfaces from Ab Initio and DFT Methods and a Summary of the MAD Computed on the Fundamental Frequencies of the Triatomic Molecules[a]

		Pure PES			Hybrid PES						
					2D-PES		3D-PES				
	1D	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T
	2D	–	Extr.DT+cc_T	Extr.DT+cc_T	MP2/TZ	M06-L/APC2	Extr.DT+cc_T	Extr.DT+cc_T	MP2/TZ	MP2/TZ	M06-L/APC2
	3D	–	–	Extr.DT+cc_T	–	–	MP2/TZ	M06-L/APC2	MP2/TZ	M06-L/APC2	M06-L/APC2
CO_2		38.9	29.1	6.1	27.8	29.8	6.1	6.1	27.6	27.5	6.7
HOF		39.9	2.6	1.9	2.5	2.8	2.0	1.9	2.4	2.6	3.5
H_2S		79.8	4.6	5.2	5.1	4.2	5.2	5.1	4.9	4.8	6.9
SO_2		12.1	5.9	5.8	5.0	5.6	5.8	5.8	4.9	4.9	5.5
HCN		80.9	48.7	6.5	57.9	47.8	6.4	7.3	8.3	9.2	5.3
HOCl		29.7	3.1	3.7	3.9	3.4	3.7	3.5	4.6	4.4	2.8
OCS		10.1	2.3	2.3	2.7	2.1	2.3	2.3	2.9	2.9	2.3
CS_2		19.0	4.5	4.6	4.7	4.7	4.6	4.6	4.8	4.8	4.8
Cl_2O		12.8	3.1	3.3	3.1	4.4	3.3	3.3	3.2	3.2	4.5
HNO		40.5	8.2	5.9	14.9	11.9	6.0	6.0	12.1	11.4	8.6
mean		34.1	7.7	4.6	8.4	8.4	4.6	4.6	5.7	5.7	5.0

[a] Vibrational calculation: VCI[gs,4]. The values are given in cm^{-1}. The truncated mean (largest and smallest values discarded) is reported for each of the PES.

TABLE 10: Potential Energy Surfaces from Ab Initio and DFT Methods and a Summary of the MAD Computed on the Fundamental Frequencies of the Tetratomic Molecules[a]

		2-D PES				3D PES	
	1D	CCSD(T)/TZ	CCSD(T)/DZ	ae-MP2/TZ	fc-MP2/TZ	M06-L/APC2	M06-L/TZ
	2D	CCSD(T)/TZ	CCSD(T)/DZ	ae-MP2/TZ	fc-MP2/TZ	M06-L/APC2	M06-L/TZ
	3D	–	–	–	–	M06-L/APC2	M06-L/TZ
H_2CO		24.8	43.5	13.3	11.1	61.1	65.5
F_2CO		8.2	37.8	10.9	9.2	15.9	17.5
Cl_2CO		5.6	16.3	11.7	12.9	20.8	21.0
average		12.8	32.5	12.0	11.1	32.6	34.7

[a] Vibrational calculation: VCI[gs,4]. The values are mean average deviations with respect to the experimental values given in cm^{-1}.

TABLE 11: Hybrid Potential Energy Surfaces from Ab Initio and DFT Methods and a Summary of the MAD Computed on the Fundamental Frequencies of the Tetratomic Molecules[a]

		1D PES		2D PES			3D PES			
	1D	Extr.DT	Extr.DT+cc_T	Extr.DT	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT	Extr.DT+cc_T	Extr.DT+cc_T	Extr.DT+cc_T
	2D	–	–	Extr.DT	Extr.DT+cc_T	M06-L/APC2	Extr.DT	Extr.DT+cc_T	M06-L/TZ	M06-L/APC2
	3D	–	–	–	–	–	M06-L/APC2	M06-L/APC2	M06-L/TZ	M06-L/APC2
H_2CO		71.8	74.1	20.4	16.1	9.7	9.5	8.8	13.5	12.5
F_2CO		19.8	20.8	6.5	5.9	6.2	6.5	5.8	6.2	6.2
Cl_2CO		7.8	8.6	4.2	6.3	6.4	4.4	5.5	5.3	5.3
average		33.1	34.5	10.4	9.4	7.4	6.8	6.7	8.3	8.0

[a] Vibrational calculation: VCI[gs,4]. The values are mean average deviations with respect to the experimental values given in cm^{-1}.

The inclusion of core correlation correction has small influences (few cm^{-1}) on all of the molecules but SO_2, where the MAD for the CC/Extr.DT and CC/Extr.DT+cc_T are 28.0 and 5.8 cm^{-1}, respectively. Even if the truncated mean after the inclusion of core correlation effects shows marginal improvements (4.6 cm^{-1}), quite remarkably, all of the error values are now smaller than 7 cm^{-1}. These data are in good agreement with the results achieved with VCI calculations on 3M-PESs constructed at the coupled cluster level of theory in the basis set limit approximation.[77]

An overview of the results obtained when DFT is used for the construction of the PES is given in Table 7. It appears in general that all of the combination xc functionals/basis sets perform roughly with the same accuracy, and the average errors are in the range of 30−50 cm^{-1} (an accuracy comparable to the one obtained with CC/DZ calculations). Despite the apparent similar performance of the xc functionals, it seems reasonable to select the M06-L as the best choice since all of the averaged errors lie in the lowest part of the range.

The triatomic molecules are the smallest systems where it is possible to construct hybrid PESs with the truncated mode-coupling expansion method. Table 8 gives an example of the type of hybrid PESs that we investigated in this survey. The values reported in the table should be compared with both the experimental values and the best ab initio estimates (i.e., CC/Extr.DT+cc_T) of Table 5, and they show the importance of the inclusion of a specific class of mode combination in the PES and the errors that one should expect when using hybrid approaches. In the specific case of HCN, it is clear that, despite a solid and elaborate ab initio procedure, the neglect of two- and three-mode couplings leads to poor results (MAD = 80.9 cm^{-1}). The inclusion of the two-mode coupling terms leads to a consistent improvement of the results (MAD = 47.8−57.9 cm^{-1}). It is worth noting that the approximation of the two-mode coupling terms afforded by the DFT approach leads, on average, to a PES of quality comparable to the ab initio one. In other terms, the anharmonicity of the potential energy surface is rather well described at the DFT level. The usefulness of the hybrid approach is demonstrated by the low MAD, corresponding to the hybrid fully coupled PESs, where the inclusion of the two-mode and three-mode coupling terms from either MP2 or DFT calculations does not deteriorate the average accuracy of the vibrational energies.

An overview of the accuracy provided by the hybrid PES for the pool of triatomic molecules is given in Table 9. Nevertheless, before investigating the performance of the multiresolution procedure for the construction of the PES, it is important to analyze the effects of the maximum level of mode combinations included in the approximate PES. The accuracy of the best ab initio PES (“Pure PES” in the first part of Table 9) is investigated as a function of the mode combination range included in the PES. When the uncoupled anharmonic potential is used, a discrepancy of 34.1 cm^{-1} is obtained with respect to the experimental results. When the two-mode coupling terms are included in the potential, the error measure drops to 7.7 cm^{-1}, demonstrating the importance of the inclusion of these couplings in the calculation of the fundamental frequencies. It is noteworthy that the further inclusion of the three-mode coupling is found to be very important for only 2 out of the 10 molecules investigated, that is, CO_2 and HCN. In the second part of the table, the performance afforded by the hybrid PES is investigated, starting with the bidimensional PES where the two-mode coupling terms are calculated at the MP2/TZ or M06-L/APC2 level. It can be observed that for most of the molecules, the accuracy achieved matches that obtained with the corresponding “pure” PES. A slightly larger error is observed for HCN when the two-mode coupling terms are calculated at the MP2 level and for HNO. Nevertheless, the overall accuracy as shown by the truncated mean is almost unaffected (8.4 versus 7.7 cm^{-1}). Concerning the hybrid PESs with account of the three-mode coupling terms, the accuracy matches that observed with pure ab initio 3D PESs when only the three-dimensional potential terms are replaced. When a more radical hybridization of the PESs is in play (i.e., when the two- and three-mode coupling terms are calculated at the MP2/TZ and/or M06-L/APC2 level), the results prove very accurate, and the truncated mean of the MADs is only 0.4 −1.1 cm^{-1} larger than the values corresponding to a purely ab initio PESs.

4.3. Tetratomic Molecules. A set consisting of three tetratomic systems was investigated, H_2CO, F_2CO, and Cl_2CO. As for the previous molecules, the calculated fundamental frequencies obtained after a VCI[gs,4] calculation have been compared with the experimental reference values as reported in the Computational Chemistry Comparison and Benchmark Database[78] (CCCBDB).

On the basis of the previous results, the PESs have been calculated by using coupled cluster, MP2 in its all-electron and frozen core approximations, and DFT adopting the M06-L xc functional. Double- and triple-ζ quality basis sets were adopted. Tables 10 and 11 report the MAD from the experimental values of the computed frequencies as a function of the method used in the construction of the PES. For this set of molecules, the expansion of the PES included only the two-mode coupling terms when ab initio methods were used, while PESs containing up to the three-mode couplings were computed with DFT.

The results obtained with a "pure" PES are reported in Table 10. The average accuracy obtained with the PES constructed at CCSD(T)/DZ level of theory is quite unsatisfactory. A consistent improvement is observed when the triple-ζ quality basis set is employed; the average MAD drops from 32.5 to 12.8 cm^{-1}. For this set of molecules, a good accuracy is observed with the PES constructed at the MP2 level, and both of the formulations (all-electron and frozen core) show an average MAD of 11−12 cm^{-1}, similar the 2M CCSD(T)/TZ results.

As a result of the xc functional/basis set screening that was carried out in the previous sections, only the M06-L functional was employed in the DFT calculations, with two triple-ζ quality basis sets. Despite the fact that the PES constructed with DFT included also the three-mode terms, the accuracy obtained is found to be quite low and, on average, slightly inferior to that obtained with a two-mode coupled PES computed at CCSD(T)/DZ.

In Table 11, the performances of various hybrid PESs are explored, starting with the simplest case where only monodimensional terms are included up to a series of three-dimensional PESs.

The inclusion of the two-mode coupling terms computed with the same level of theory (Extr.DT and Extr.DT+cc_T) improves considerably the accuracy obtained compared to that of the pure 1D PESs, and the average MAD drops under the values observed with the CCSD(T)/TZ PES of Table 10. The core correlation effect computed at the MP2 level of theory is found to account for 1 cm^{-1} on the average.

We finally explore another way to construct two-mode coupled hybrid PESs, where the monodimensional terms from the ab initio extrapolation procedure have been combined with the higher mode-coupling terms obtained at the DFT level. As observed for the triatomic molecules, despite the limited accuracy obtained from the purely DFT PESs, the anharmonic coupling terms are found to be quite accurate, and their inclusion in the hybrid formulation gives rise to potentials that are found to be quite competitive with the ab initio ones.

Following the same philosophy, a series of hybrid PESs with the inclusion of three-mode coupling including terms computed both with the extrapolative ab initio formulation and DFT has been constructed. The overall accuracy of these potentials is found to be rather good, and the average MAD is found consistently smaller than 10 cm^{-1}.

5. Summary and Outlook

The multiresolution adaptive density-guided approach (MADGA) for the construction of potential energy surfaces to be used in vibrational structure calculations has been implemented and tested.

The flexibility of the machinery allows an automatic generation of hybrid PESs that may include basis set extrapolation, core correlation correction, and, in principle, all types of linear corrections. Furthermore, the intrinsic mode-coupling formalism is available, meaning that mode couplings computed with different methods can be easily combined.

In this article, the MADGA was used to perform a systematic survey of the accuracy of the PES constructed with different types of approximations for a set of 20 molecules ranging from diatomic to the tetratomic systems.

The statistical analysis of the accuracy obtained when the PESs were used in vibrational structure calculations provided useful insight on the "art" of PES construction for vibrational calculations, and some rules of thumb have been devised:

- The inclusion of the basis set extrapolation for the correlated ab initio methods gives a PES whose quality is superior to the one of the parental PESs.
- MP2 estimations of the core correlation effects are found to be fairly precise, and for specific cases, for example, SO_2, the inclusion of these effects provides a significant improvement of the results.
- In an attempt to achieve spectroscopic accuracy, at least the two-mode coupling terms must be included in the restricted mode expansion of the fully coupled PES. A good strategy is to combine the best monodimensional or bidimensional anharmonic ab initio PES with higher mode couplings calculated at a lower electronic structure level, such as DFT.
- Despite the relative inaccuracy of DFT in the calculation of harmonic frequencies and of the monodimensional anharmonic part of the potential, the higher dimensional PEFs are rather well described and may be used in the intrinsic restricted mode-coupling expansion of the PES to correct ab initio PESs with a marginal loss of accuracy.

Future work will concentrate on the design of a suitable strategy for an efficient prescreening of the important mode-coupling terms in the potential based on information of vibrational density and the combination of the ADGA with the use of low-order derivatives.

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Supporting Information Available: Complete set of data (calculated and experimental frequencies) for the 20 molecules considered in the survey. This material is available free of charge via the Internet at http://pubs.acs.org.

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