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REGULAR ARTICLE

# A local-MP2 approach to the ab initio study of electron correlation in crystals and to the simulation of vibrational spectra: the case of Ice XI

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**Abstract** Wave-function-based computational techniques for describing electron correlation effects in periodic systems have a long history. Among early attempts, the method proposed by Colle and Salvetti (Theor Chim Acta 37:329, 1975) more than 30 years ago is noteworthy for its simplicity, power, and far-reaching consequences. The renewed interest in this topic is due to the well-known failure of techniques based on Density Functional Theory when it comes to obtaining very accurate estimates of some important quantities. Here we present the essential features of an ab initio code, (`CRYSCOR`) recently implemented (Phys Rev B 76: 075101, 075102, 2007), which solves the MP2 equations for crystals by adopting a local-correlation approach and using as a reference the Hartree-Fock solution provided by the `CRYSTAL` program. As an example of application, we discuss the MP2 corrections to the frequency of some vibrational modes in a proton-ordered structure of water ice (Ice XI).

**Keywords** Ab initio · Local correlation · MP2 · Crystal · Vibrational frequencies · Ice XI

## 1 Introduction

A post-Hartree-Fock (HF) computational scheme for describing the electronic properties of non-conducting crystals (`CRYSCOR`) has been recently presented [1–5]. Using as a zero approximation the solution provided by the `CRYSTAL` program [6], it solves the perturbative problem at second order (MP2), by adopting a local-correlation approach [7]. The motivations for this effort are exposed in Sect. 2 in a historical perspective. The essential aspects of the new technique and its present capabilities are recalled in Sect. 3. As an example of its possible use, we analyze in Sect. 4 the MP2 corrections to the frequency of some vibrational modes in a proton-ordered structure of ordinary ice (Ice XI). The results are critically compared to those obtained using DFT. Some prospects of future developments are outlined in Sect. 5.

## 2 Post-Hartree-Fock techniques for crystals: a historical perspective

For more than two decades, computational techniques based on Density Functional Theory (DFT) in the Kohn–Sham formulation [8] have dominated the field of simulation studies concerning the electronic properties of condensed systems. This resulted from a lucky combination of successful ingredients: (a) the power of the one-electron Kohn–Sham Hamiltonian and of its generalizations (DFT response theory); (b) the use therein of exchange-correlation functionals progressively better calibrated; (c) the restriction of the problem to the valence electrons, which justifies the adoption of a basis set (BS) of plane waves in combination with suitable pseudopotentials for the core electrons, and (d) the simplicity and generality

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of the resulting codes, such as `VASP` [9, 10]. Furthermore, the Car-Parrinello technique [11] has opened the possibility to incorporate economically in this kind of programs the so-called ab initio molecular dynamics, a tool providing extremely valuable information in a wide spectrum of solid-state problems.

Another route was possible, consisting in the generalization to crystalline systems of wave-function-based techniques as were and are practised in molecular quantum chemistry. The group of Theoretical Chemistry in Torino has been among the pioneers of this alternative route: after about 10 years of preparatory work in collaboration with Saunders of the Daresbury Laboratories, our `CRYSTAL` program appeared in 1988 as the first public HF code for periodic systems [12, 13]. It was modeled to some extent on Pople's `Gaussian82` code [14, 15] from which it took over the use of Gaussian-type functions (GTF) as BS and some of the related algorithms; however, many new ideas had been introduced for exploiting translational and point symmetry, and for evaluating approximately or truncating efficiently the infinite lattice sums. From that early version to the newest one [6], the code has been improved enormously (in particular, DFT techniques have been implemented), but its basic features have remained essentially the same. Because of its special characteristics, `CRYSTAL` has enjoyed a moderate but standing success among workers in the field. Let us just mention the fact that the strict similarity between this periodic program and standard molecular codes permits their combined use not only for obtaining reference energies, but also for estimating the effects of an upscaling of the quality of the calculation using ONIOM-like techniques [16–18].

However, `CRYSTAL`'s most noteworthy peculiarity, i.e., its ability to solve (approximately) the HF equations, has been felt for many years as a practically useless feature, except for allowing `CRYSTAL` to add a fraction of "exact exchange" to the local DFT functionals, as required by the successful "hybrid exchange" techniques [19] (again, a first-time achievement among periodic codes). As a matter of fact, HF is *conceptually* important, since it occupies the lowest rank in the hierarchy of wave-function based methods which allow us to study non-empirically various properties of many-electron systems: the ascent along this hierarchy rigorously and systematically improves the accuracy, which is not possible in the frame of DFT. On the other hand, HF does not cover the effects of electron Coulomb correlation: though relatively small, these effects are often of decisive importance for a correct individualization of the stable structures and for the accurate description of reactive processes; furthermore (in spite of Koopmans' theorem), one-electron HF eigenvalues are usually a poor approximation of ionization and electron affinity energies. This is not only true for molecules but also for condensed systems as well: in this case, the attention is often more concentrated on band structures rather than on total ground-state energy and related electronic properties. The failure of the HF description in this respect, concerning in particular the free-electron gas, is well known and has often been over-emphasized. It can be noted that the lack in HF of adjustable parameters (at variance with the wide spectrum of exchange-correlation formulae practiced in DFT) may have added to its scarce attractiveness. On the other hand, climbing the ladder of progressively more accurate techniques, even just up to the next step (MP2), is very costly, especially for periodic structures. For many years, pioneering attempts in this respect have been limited to extremely simple systems, for instance, the one-dimensional hydrogen chain [20].

The Colle-Salvetti technique, proposed in the mid seventies and progressively improved [21–23], offered to some extent a way out of these difficulties. It was a brilliant shortcut for estimating approximately, but accurately, the correlation effects on ground-state energies and excitation energies. What was particularly interesting about it, is that it was formulated in the spirit of wave-function based methods, by introducing a reasonable Ansatz as concerns the modified form of the two-electron density matrix with respect to that provided by the reference HF calculation. Through a series of well-argumented approximations, working formulae were obtained, easy to use and containing a minimum amount of parametrization. It is not the case here to remember the far reaching consequences of that approach: the restatement of the Colle-Salvetti formula by Lee, Yang and Parr in the frame of DFT [24], has resulted in one of the most successful correlation functionals ever proposed. Rather, we would like to recall the fruitful interaction that has taken place between Salvetti's group and ours in Torino, to introduce that technique in `CRYSTAL` [25, 26]. The results were quite satisfactory for a number of systems of different nature [25–28], and competitive with those obtained using DFT approaches.

Something has changed in the very last years in the domain of computational techniques for "large" systems (big molecules or periodic structures). With the explosively growing power of computer facilities and the increasing sophistication of simulation tools, new requirements are being formulated, and new routes begin to be explored. On the one hand, the limitations of DFT approaches have often become evident, due to their inability to describe weak interactions (dispersive forces), their overestimation of transition state energies, their underestimation of the energies of excited states with a charge-transfer character, etc. On the other hand, the power and accuracy of *N*-scaling wave-function-based local-correlation techniques, as implemented for instance in the `MOLPRO` program [29], have been convincingly demonstrated in the molecular context [30– 32]. Dynamical correlation is not a long-range effect as compared to Coulomb interactions, already treated at the HF level. The $\mathcal{O}(N^5)$ scaling of canonical MP2 method or $\mathcal{O}(N^6)$ of coupled cluster (CCSD) approaches is caused by the use of non-local, canonical molecular orbitals. These orbitals diagonalize the Fock matrix, which considerably simplifies the formalism of the post-HF correlation schemes; on the other hand, their delocalized structure prevents the short-range nature of dynamic correlation to be exploited. The reverse occurs, in a sense, when spatially localized orbitals are used [33].

Precisely for these reasons, there is a renewed interest in wave-function-based methods even in the field of solid state physics. While referring to a recent publication [4] for a detailed account of existing literature, we just want here to mention some of the most interesting techniques currently explored and tested.

Fulde, Stollhoff and coworkers have pioneered the studies of electron correlation in solids using local approaches, by developing a technique which can be applied both to insulating and conducting systems [34–36]. An orbital invariant formalism for MP2, based on the Laplace transform of the energy denominators [37], has been applied to systems, periodic in one and two dimensions, by Ayala et al. [38] in an atomic orbital AO representation. Förner and coworkers developed local CC theory for extended one-dimensional systems [39] which allowed them to recover most of the correlation energy; they used for this purpose mutually orthogonal Wannier functions (WF) [40], obtained as a Fourier transformation of occupied and virtual Bloch states. Flocke and Bartlett suggested a method where the correlation energy of crystals at the CC level is estimated using natural bond orbitals, obtained for a set of small subunits of the given structure [41]. Similar ideas are used in Stoll's incremental scheme [42], where the correlation effects are calculated through a many-body expansion in terms of groups of localized orbitals. In the post-HF part of the calculation, the infinite crystal is modeled as a large enough cluster and the $n$-body terms of the expansion contain the contributions of correlation among different sets of $n$ orbitals. Applications of the incremental scheme cover a large class of systems and for many of them represent the best solution presently available. The case of the ionic crystals can be cited as an example [43].

## 3 The `CRYSCOR` program

In spite of these efforts, no code yet exists for the ab initio treatment of correlation effects in crystals characterized by generality, robustness, and user-friendliness. A few years ago, some of the present authors together with the group of professor Schütz of the University of Regensburg started the `CRYSCOR` project with precisely this aim. Our approach is based on the local correlation scheme originally proposed for molecules by Pulay and Saebø [7] and further developed by Werner, Schütz et al. [30–32]. At present, `CRYSCOR` solves the local-MP2 (LMP2) equations for non-conducting, non-spin-polarized crystals, using as a reference the HF wave-function provided by the LCAO periodic code `CRYSTAL` in a BS of GTFs, $\{\phi_\mu\}$ [6]. Note that the quality of the computation finally depends on that of the BS. The latter cannot be chosen at will, because too diffuse functions can cause instabilities in the HF-SCF procedure [12, 13]. However, a number of GTFs can be included a posteriori on top of those used in the `CRYSTAL` calculation (the so-called "dual" BS), to improve the description of the virtual manifold. The main characteristics of `CRYSCOR` and its present capabilities are outlined below.

### 3.1 Basic features and computational parameters

### *3.1.1 The local functions and their truncation*

Following Pulay's ideas [7], local functions are used in our LMP2 method to span the occupied and virtual manifolds of the HF reference. For the former, orthonormal WFs are used (to be denoted as **i**, **j**, etc.) which are generated by `CRYSTAL` from the canonical occupied Bloch orbitals using the scheme devised by Zicovich-Wilson et al. [44]. For the latter, we use the so-called projected atomic orbitals (PAO), denoted **a**, **b**, etc., which result from the projection of the occupied space out of the $\phi_\mu$'s; PAOs form a redundant nonorthogonal set, but are appreciably well localized.

Both WFs and PAOs are expressed as a linear combination of the $\phi_\mu$'s, in principle extended to infinity. A crucial issue is then the truncation of their tails. Two parameters, `tolw` and `tolp`, are set from input such that all terms in the linear combination are neglected whose coefficients are less, in absolute value, than the respective tolerances. A value `tolw` = `tolp` = 0.0001 is recommended.

### *3.1.2 The use of translational and point symmetry*

While symmetry is practically irrelevant for big molecules, it is of fundamental importance for periodic structures. `CRYSTAL` provides our program with all the needed information concerning translational and point-group symmetry of the system. It also symmetrizes the WFs owing to the procedure proposed by Casassa et al. [45] PAOs have by construction the symmetry of the parent GTFs. We note in particular that all WFs and PAOs can be generated through lattice translations from those formally attributed to the reference zero cell, which are in a number of $N/2$ and $M$, respectively, $N$ being the number of electrons and $M$ the number of AOs per unit cell. The full exploitation of symmetry is an essential feature of our method: it permits us to reduce the computational effort to irreducible quantities.

### *3.1.3 The LMP2 equations: use of the locality Ansatz*

The orbital invariant MP2 energy per unit cell in the local approximation is given by the following expression:

$$E^{\mathrm{LMP2}} = \sum_{(\mathbf{i}\in 0\ \mathrm{cell})} \sum_{(\mathbf{j}\ \mathrm{near}\ \mathbf{i})} E^{\mathrm{LMP2}}_{\mathbf{i},\mathbf{j}} \tag{1}$$

$$E^{\mathrm{LMP2}}_{\mathbf{i},\mathbf{j}} = \sum_{(\mathbf{a},\mathbf{b})\in[\mathbf{i},\mathbf{j}]} K^{\mathbf{i},\mathbf{j}}_{\mathbf{a},\mathbf{b}} \left(2T^{\mathbf{i},\mathbf{j}}_{\mathbf{a},\mathbf{b}} - T^{\mathbf{i},\mathbf{j}}_{\mathbf{b},\mathbf{a}}\right) \tag{2}$$

Here $K^{\mathbf{i},\mathbf{j}}_{\mathbf{a},\mathbf{b}} \equiv (\mathbf{i},\mathbf{a}|\mathbf{j},\mathbf{b})$ are the electron repulsion integrals (ERI) between two WF–PAO product distributions (PD), and $T^{\mathbf{i},\mathbf{j}}_{\mathbf{b},\mathbf{a}}$ are the excitation amplitudes, which are determined by solving self-consistently the LMP2 equations [1].

The limitation of the first sum of equation (1) reflects the use of translational symmetry; in fact, the calculation is restricted to the symmetry-irreducible WF pairs with the first WF in the zero cell. The truncation of the other sums corresponds to the use of the locality Ansatz. Consider first equation (2). For a given pair of WFs **i** and **j**, the excitation space is confined to their spatial vicinity, or in other words, to the so-called domain [**ij**], which is the union of the domains of the two WFs. This means that the amplitudes $T^{\mathbf{ij}}_{\mathbf{ab}}$ are assumed to be non-zero only if PAOs **a** and **b** are spatially close to WFs **i** and/or **j**. On the other hand, as indicated by the second sum in Eq. (1), the centers of the two WFs must be relatively close to each other; otherwise, the corresponding "pair energy" $E^{2}_{\mathbf{i},\mathbf{j}}$ is negligibly small. In summary, the local approximation is described by two parameters: the domain size $S$ of each WF and $D$, the maximum distance between two WFs beyond which pair energies are neglected. The overall scaling is then proportional to $n$, the size of the irreducible portion of the crystal unit cell.

Typically, the domain of a WF includes all PAOs that belong to first and second neighbors about its center; $D$ is usually set to 8/12 Å.

### *3.1.4 Evaluation of ERIs and extrapolation to infinity*

The evaluation of the ERIs in the $\{\phi_\mu\}$ set and their four-index transformation into the WF–PAO basis (see Eq. 2) is so demanding computationally that no accurate calculation for systems of real interest is feasible; their approximate evaluation is then mandatory. For this purpose, WF pairs (**i, j**) are first classified according to the distance $d_{\mathbf{ij}}$ between their centers into "strong+weak" ("close-by") pairs $(0 \le d_{\mathbf{ij}} < d_1)$ and "distant" pairs $(d_1 \le d_{\mathbf{ij}} < D)$. For integrals related to close-by pairs, the density-fitting-periodic (DFP) technique is used, while distant pairs are treated in a multipolar approximation. The analytic evaluation of integrals is always feasible for calibration purposes.

The density fitting technique for calculating ERIs in a molecular context has a long and successful history [46–48]. It implies the expansion of PDs in a BS of auxiliary fitting functions, $\{\Phi_P\}$, which can be either GTFs or Poisson functions, the Laplacian of GTFs [49]. DFP represents its extension to periodic systems, and is characterized by two special features with respect to its molecular counterpart [2, 3]: (i) the systematic use of reciprocal space techniques; (ii) the careful handling of long-range interactions, via a separate technique for evaluating the coefficients in the expansion of fitting functions of GTF type (which are few in number, but have non-zero multipoles) and of Poisson-function type (which are the large majority of the fitting set, but exhibit fast decay and have no multipoles to any order). DFP has been shown to be very accurate and efficient, with gains of one to three orders of magnitude in computational times with respect to the analytic evaluation of the integrals.

For distant pairs, the two WF–PAO PDs are essentially external to each other, and a multipolar technique can safely be used. After evaluating the multipoles of each PD about the respective WF center up to a maximum order ($L$), the ERI is estimated as the Coulomb interaction between the multipoles of the two PDs.

Neglecting pairs beyond $D$ is crucial for limiting the number of excitation amplitudes needed (see Eq. 3), and so to insure the required $n$-scaling. However, due to the compact nature of 3-d crystals, the missing contribution to $E^{\mathrm{LMP2}}$ from those "very distant" pairs, $E^{\mathrm{out}}$, only decays as $D^{-3}$. An accurate zero-cost estimate of $E^{\mathrm{out}}$ is possible after considering that at large distances pair energies follow the London $d_{\mathbf{ij}}^{-6}$ law as is present in the well-known 6-12 Lennard-Jones (LJ) expression. By exploiting translational symmetry, the LJ parameters for each type of pair are obtained from the pair energies explicitly calculated up to $D$, and the corresponding contribution is then extrapolated from $D$ to infinity [4].

The main parameters involved and their standard settings are as follows. The separation $d_1$ between close-by and distant pairs is set to 6–8 Å. An adequate shrinking factor for reciprocal-space techniques in DFP turns out usually to be the same as in `CRYSTAL`'s SCF procedure. The $\{\Phi_P\}$ set of fitting functions can be taken from a library, based on `MOLPRO`, but adapted and complemented for use with periodic systems; triple-zeta quality sets are usually adequate. In the multipolar calculation for distant pairs, the maximum order of multipoles, $L$, is set to four by default.

### 3.2 A summary of `CRYSCOR` capabilities

In principle, any system translationally periodic in 3 (ordinary crystals), 2 (slabs), 1 (polymers), and 0 (molecules) dimensions can be treated, provided that their closed-shell HF solution is a reasonable reference. As anticipated, the choice of the $\{\phi_\mu\}$ BS is a critical issue for two main reasons: first, one must be sure that the `CRYSTAL` calculation is feasible which prevents the use of very diffuse GTFs; second, an acceptable description of the lower portion of the virtual manifold should be achieved. Work is going on to make progress in both directions, also by exploiting the dual basis option (see Sect. 3), and to set up a library of computationally reasonable $\{\phi_\mu\}$ sets. Among calculated properties, the energy $E^{\mathrm{LMP2}}$ is of course the most important. In this respect, the following should be noted.

(i) Very often, the quantity of interest is the formation energy $E^f$ of the crystal from some ““reactants” (atoms, ions, molecules,…). In calculating the difference, it is important to account for the basis-set-superposition-error (BSSE) when incomplete BSs are used. As concerns the LMP2 contribution to $E^f$, an easy solution to this problem has been proposed, i.e., the so-called partition method [50], which consists in estimating $E^{\mathrm{f,LMP2}}$ directly from Eq. (3) by excluding those WF pairs where both $\mathbf{i}$ and $\mathbf{j}$ belong to the same reactant. This technique must, however, be used with some caution, because it tends to slightly underestimate the BSSE, contrary to the standard counterpoise technique which usually underestimates it [51, 52].

(ii) Another important class of problems concerns the evaluation of the correlation correction to the *interaction energy* between two subsystems $A$ and $B$ (for instance, between adsorbed molecules and a periodic substrate). Again, it is possible to restrict the calculation to WF pairs with $\mathbf{i} \in A, \mathbf{j} \in B$, with enormous savings in time [4].

(iii) Studying the dependence of the total electronic energy on the displacement of nuclear coordinates from the equilibrium configuration permits us to evaluate correlation effects on elastic constants and on vibrational frequencies (for the latter case, see Sect. 4).

(iv) `CRYSCOR` calculates (at zero cost) Grimme's spin-component-scaled estimate of the MP2 correlation energy [53, 54]; this formula seems very effective in molecules, but is still to be systematically tested in crystals.

Apart from energy, `CRYSCOR` allows us to obtain the correlation correction to the one-electron density matrix according to two different schemes [55–57]. This feature is potentially important because very accurate experimental information is available on the density matrix of many crystalline systems via directional Compton profiles and X-ray structure factors [58].

Computational times heavily depend on the complexity of the system and on the tolerances adopted. The two examples below are referred to single-point computations performed on an Opteron 2.2 GHz single processor, 4 GB memory:

(a) *fcc* argon (1 atom per cell; [4*s*4*p*3*d*1*f*] BS; 13-atom WF domains; $d_1 = 6$ Å; $D = 12$ Å; 36 irreducible WF pairs; `tolw` = `tolp` = 0.0001): **38,000** CPU s [52].

(b) Ice XI (12 atoms per cell, [$6-311G(p,d)$] BS; molecular WF domains; $d_1 = 6$ Å; $D = 12$ Å; 1,003 irreducible WF pairs; `tolw` = `tolp` = 0.0001): **6,500** CPU s [59].

The difference in computational times must be traced back to the fact that much larger WF domains have been used in the former case (13 atoms) than in the latter (3 atoms).

## 4 Vibrational frequencies in crystals: the case of Ice XI

Detailed information about many crystalline systems (e.g., molecular crystals) can be obtained from vibrational spectroscopy and, in the case of systems with hydrogen atoms, from inelastic incoherent neutron scattering (IINS) experiments. The comparison between experimental spectra and those obtained by ab initio computations is of great help for the interpretation of the vibrational modes and for the calibration of the theoretical tool.

In the frame of the Born-Oppenheimer separation of nuclear from electronic motions, the harmonic approximation usually provides a reasonable guess of vibrational frequencies; in `CRYSTAL` it is adopted for calculating the "optical" ones (those at the zone center) according to the standard procedure [60]. The mass weighted matrix $V$ of the second derivatives of the electronic energy per cell with respect to the displacements of the $M$ nuclei in the unit cell from the equilibrium configuration $\mathbf{R}_0$ is diagonalized ($\Lambda = U^{-1}VU$). This permits the identification of $3M$ independent vibrational modes, each characterized by a harmonic frequency $\nu_k^0 = \sqrt{\lambda_k}$; the eigenvector $\mathbf{U}_k$ describes the corresponding nuclear motion as a function of the 1D normal coordinate $Q : \mathbf{R}^k(Q) = \mathbf{R}_0 + (Q\lambda_k^{1}/4)\mathbf{U}_k$. The accuracy of such estimates rests not only on the validity of the harmonic approximation for separating the nuclear motions from each other, but also on the technique used for evaluating the electronic energy, and on the hypothesis that the dependence of the electronic energy on $Q$ is well described by a parabolic behavior beyond a strict vicinity of the equilibrium. Let us retain the first approximation (the independence of modes), and consider the 1D Schrödinger equation for the $k$-th mode:

$$\hat{h}^k_{Y/X}|\psi^k_n(Q)\rangle = \varepsilon^k_n|\psi^k_n(Q)\rangle$$

$$\hat{h}^k_{Y/X} = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}Q^2} + W^k_{Y/X}(Q) \qquad (3)$$

Here, $Y$ indicates the method adopted for finding the equilibrium configuration $\mathbf{R}_{0,Y}$ and for separating the modes using the corresponding $V_Y$ matrix, while $X$ specifies the technique employed for calculating the energy at a given configuration. So, $W^k_{Y/X}(Q)$ is the difference between the "$X$" electronic energies calculated at the nuclear configurations $\mathbf{R}^k_Y(Q)$ and $\mathbf{R}_{0,Y}$.

$X$ may be different from $Y$: the case where $Y$ is the hybrid B3LYP technique [19] while $X$ is HF+LMP2 is treated below for the case of Ice XI. The problem here is that `CRYSCOR` does not yet calculate the analytic energy gradients; therefore, an accurate estimate of the equilibrium configuration $\mathbf{R}_{0,X}$ and of the corresponding mass-weighted Hessian matrix $V_X$ (with $X = \mathrm{HF} + \mathrm{LMP2}$) is practically unfeasible. On the other hand, it is known that B3LYP generally provides a description of the equilibrium configuration and of the vibrational spectrum in good agreement with the experiment. This is true in the case of Ice XI as proved in a forthcoming publication. Therefore, $\mathbf{R}_{0,Y}$ and $V_Y$ from `CRYSTAL` (with $Y =$ B3LYP) can serve as a reference for individualizing the different modes and for estimating the HF+MP2 frequencies from the corresponding $W^k_{Y/X}$ curves. The validity of this procedure will be checked a posteriori.

After choosing a mode ($k$), we can calculate a number of values $W^k_{Y/X}(Q)$ (e.g., for $Q$ regularly spaced between $\pm 2\lambda_k^{1}/4$), and perform a polynomial fit of such data. Equation (1) can then be solved numerically with the desired accuracy using the numerical method proposed by Lindberg [61] and implemented by Ugliengo in the `ANHARM` code [62]. For finite $Q$, the function $W^k_{Y/X}(Q)$ depends on the set of coordinates used to represent the eigenvector $\mathbf{U}_k$. In the present implementation we have limited ourselves to considering Cartesian coordinates. Work is in progress to allow other choices to be adopted (for instance, internal coordinates) and, more fundamentally, to go beyond the independent-mode approximation through an extension to periodic systems of techniques successfully introduced in a molecular context [63, 64]. The approach just described is applied below to some modes of Ice XI (Ref. [65] for the whole set of librational modes).

Water ice is the prototype of hydrogen-bonded systems; Ice XI is its only proton-ordered polymorph which is stable at zero pressure [66]. It is a ferroelectric crystal of space group $Cmc2_1$ [67, 68]; the reason for its peculiar stability is not completely understood yet. A detailed computational study recently performed with two types of DFT Hamiltonians and using 16 different models of proton-ordered ice [69], indicate $Cmc2_1$ to be the most stable structure. This important result is not conclusive, since DFT is known to generally provide a poor description of long range dispersive interactions. New clues could be found by considering the effects of electron correlation corrections; in a parallel study [59] based on `CRYSTAL` + `CRYSCOR` calculations we have critically re-considered the problem of the relative stability of different Ice structures, already tackled by us in past years [70]. Special attention has been devoted to exploring the effect of electronic correlation on the vibrational frequencies, following the scheme just outlined. Here we concentrate on a few specific modes, which will permit us to provide more details on some computational aspects. All calculations described below have been performed using the same 6-311$G(p,d)$ BS as in our previous study [70]. The region of the vibrational spectrum of Ice most affected by proton ordering is the librational one as first found by Li et al. by means of IINS on a partially

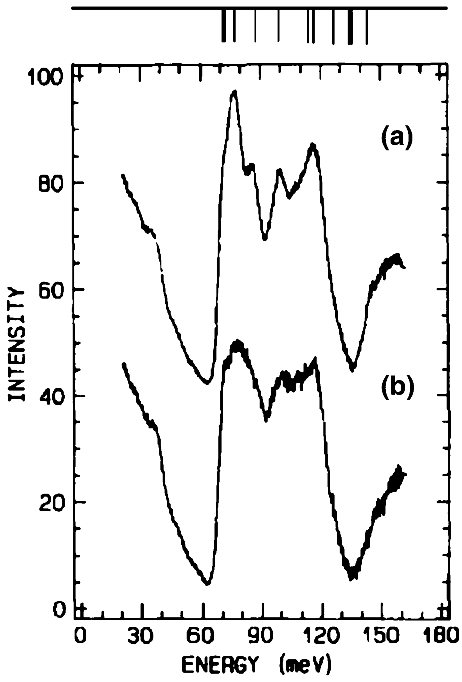


**Fig. 1** IINS spectra [71] of Ice XI (**a**) and of ordinary ice (**b**) in the librational region. The calculated (B3LYP) librational harmonic frequencies of Ice XI are reported on top

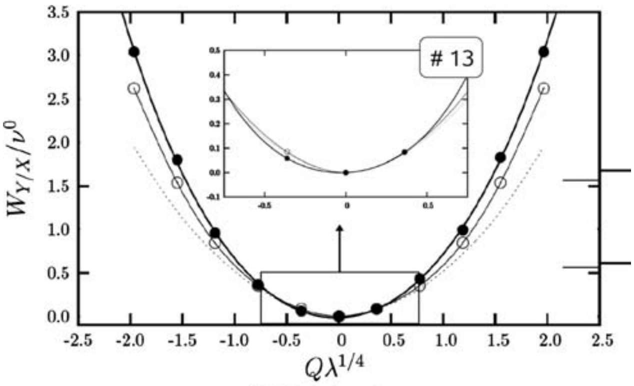
transformed specimen (see Fig. 1; [71]), and confirmed recently by Raman measurements [72]. The B3LYP treatment of the harmonic problem with `CRYSTAL` permits us to individualize 12 librational modes (#13 to #24) in the region 586/1,153 cm$^{-1}$ (73/143 meV), largely coinciding with the experimental one (see Fig. 1). These modes are a combination of three types of oscillation of the almost rigid molecule about the three orthogonal axes through the oxygen atom: about $z$, the perpendicular to the molecular plane in its equilibrium position (conventionally called "rocking"); about $x$, the symmetry axis ("twisting"); about $y$ ("wagging"). They can be visualized by looking at the animations available on the web [73]. We consider here three of these modes (#13, #17, #23), which can be assigned to the first, second, and fourth peak of the experimental spectrum, centered at 79, 88, and 116 meV, respectively [71]. Table 1 reports some numerical results concerning the three selected modes; Fig. 2 provides pictorial information about the limits of the harmonic approximation and about the adequacy of the procedure adopted for estimating the correlated frequencies. In the following, we briefly comment on these data.

The HF harmonic frequencies in the librational region are appreciably red-shifted with respect to the experiment, especially at the lowest frequencies. This is to be expected: HF overestimates the intra-molecular OH bond and underestimates the intermolecular O–H one; as a matter of fact, the HF optimized values of $d_{\mathrm{OH}}$ and of $d_{\mathrm{O-H}}$ are 0.953 and 1.948 Å, to be compared to the respective experimental values of 0.985 and 1.779 Å. Not surprisingly then, the second derivatives of the energy with respect to the librational coordinates are too small. The anharmonicity

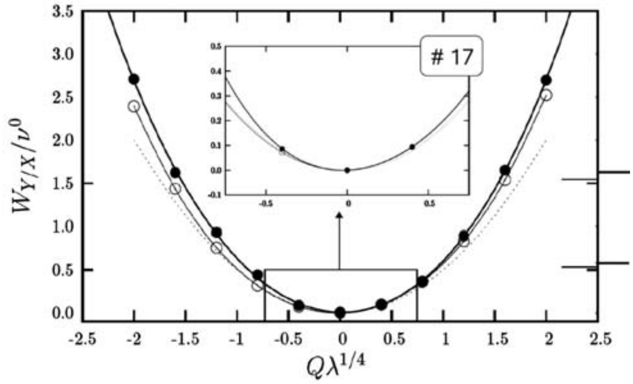
**Table 1** First two eigenvalues $(\varepsilon_0, \varepsilon_1)$ of the vibrational Hamiltonian $h^k_{Y/X}$ (Eq. 3) and first transition energy $(\omega_{01} = \varepsilon_1 - \varepsilon_0)$ of Ice XI, for three $k$ modes and three $Y/X$ techniques as indicated

| $Y$ | HF | | B3LYP | | B3LYP |
|---|---|---|---|---|---|
| $X$ | HF | | B3LYP | | HF+LMP2 |
| Mode #13 | | | | | |
| $\varepsilon_0$ | (30.25) | 34.13 | (36.35) | 39.97 | 42.94 |
| $\varepsilon_1$ | (90.76) | 107.80 | (109.05) | 123.53 | 132.50 |
| $\omega_{01}$ | (60.51) | 73.67 | (72.70) | 83.56 | 89.56 |
| $\gamma$ | 21.7% | | 14.9% | | |
| Mode #17 | | | | | |
| $\varepsilon_0$ | (36.80) | 40.07 | (44.05) | 46.27 | 49.41 |
| $\varepsilon_1$ | (110.41) | 124.62 | (132.14) | 141.43 | 149.95 |
| $\omega_{01}$ | (73.61) | 84.55 | (88.09) | 95.16 | 100.54 |
| $\gamma$ | 14.9% | | 8.0% | | |
| Mode #23 | | | | | |
| $\varepsilon_0$ | (59.28) | 59.97 | (67.79) | 68.36 | 70.33 |
| $\varepsilon_1$ | (177.84) | 181.36 | (203.39) | 206.10 | 210.30 |
| $\omega_{01}$ | (118.56) | 121.39 | (135.60) | 137.74 | 139.97 |
| $\gamma$ | 2.4% | | 1.6% | | |

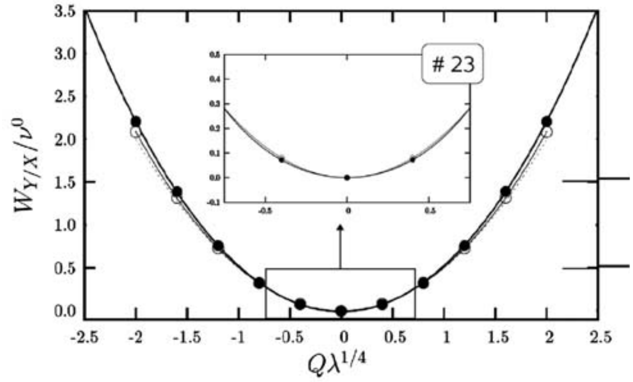
For $X = Y$ = B3LYP or HF, the harmonic estimate (in parentheses) and the anharmonicity percentage $\gamma = 100(\omega^{\mathrm{anh}}_{01} - \omega^{\mathrm{h}}_{01})/\omega^{\mathrm{h}}_{01}$ are also provided. All data in meV (1 meV = $3.675 \cdot 10^{-5}$ Hartree = 8.065 cm$^{-1}$)



**(a)** Mode #13



**(b)** Mode #17



**(c)** Mode #23

**Fig. 2** Potential curves $W^k_{Y/X}(Q)$ for the three selected modes (see Eq. 1), with $Y$=B3LYP, and $X$ either B3LYP (thin continuous line, open circles), or HF+LMP2 (thick continuous line, full circles). The harmonic B3LYP approximation is drawn as a dotted line. Scaled coordinates are used for the $x$ and $y$ axis. The first two anharmonic levels are drawn on the right (inside the frame for B3LYP, outside it for HF+LMP2), to be compared with the harmonic ones, $0.5\nu_0$ and $1.5\nu_0$

corrections are seen to act in the sense of shifting all frequencies upwards: this is apparently associated with the onset of strong inter-molecular repulsions for large displacements along the librational normal coordinates. Since the entity of the correction strongly decreases when passing from the bottom to the top of the band, the net result is a general blue-shift with a decrease of the bandwidth. The anharmonic HF frequencies come so in rather good agreement with the experiment: this could, however, be the result of a lucky cancellation of errors, given the poor description of the ice structure at this level of approximation. As it is seen in Fig. 1, the B3LYP harmonic spectrum in this region is much closer to the experiment, which corresponds to the good energetic and structural description of Ice XI provided by this approximation. The data of Table 1 show that the anharmonic corrections act qualitatively as in the HF case, although they are less important in percentage. The reasons for the departure from harmonicity seem, however, to be different in this case. An analysis of mode #13 shows that the molecule is appreciably deformed at 1.6 times the classical elongation ($d_{\mathrm{OH}}$ is increased by 0.9%, $\widehat{\mathrm{HOH}}$ decreased by 0.3% with respect to the equilibrium configuration), which means that anharmonicity is here strictly related to the deviation from the ideal *rigid-molecule* behavior. On the whole, the anharmonic B3LYP spectrum turns out to be quite similar to the experimental librational one both as concerns distribution of peaks and band-width, although blue-shifted by about 10 meV on average.

Consider finally the B3LYP/HF + MP2 results. As seen in Table 1, they are about as good as the B3LYP/B3LYP ones. Figure 2, which reports the calculated $W^k_{Y/X}(Q)$ values (dots) and the interpolating curves for the three selected modes and the two techniques, permits us to introduce further considerations about the present results. The departure from the harmonic behavior (dotted curve) is particularly evident for the two low-energy modes, and it is seen to be appreciable already within the classical elongation $(-1 < Q\lambda_k^{1/4} < 1)$. For mode #17, the two techniques provide results which are qualitatively different: the B3LYP/B3LYP curve is considerably more asymmetric, the departure from harmonicity being much larger in the direction of "positive" $Q$'s, which is found to correspond to enhanced deformation of the water molecules; instead, the B3LYP/HF+MP2 curve resembles rather to a constrained elastic oscillation of the individual molecules in the repulsive field of the surrounding ones. On the other hand, for all three modes, the latter curve is very close to the B3LYP/B3LYP one in a strict neighborhood of $Q = 0$, which provides some support *a posteriori* to the procedure adopted, in the sense that it can be expected that the equilibrium geometry at the ab initio correlated level, and also the Hessian matrix of the nuclear motions should be similar to the B3LYP/B3LYP (and therefore to the experimental) ones. This fact in itself is very encouraging, if one considers the inadequacy of the zero-order HF approximation.

Anyhow, the analytic calculation of the MP2 first derivatives of energy will permit us in a near future to get rid of the partial inconsistency of the present technique for the evaluation of the vibrational frequencies. Another important step would be to estimate the influence of the coupling of quasi-degenerate modes on the anharmonicity corrections [64].

## 5 Conclusions and prospects

A standard version of `CRYSCOR` with the capabilities here described is presently being prepared, tested, and documented; it will be distributed publicly with `CRYSTAL` in the near future. At the same time, work is going on in order to improve its performance, to add new features and to explore new possibilities. An estimate of the optical excitation energies via a configuration interaction (singles) scheme is our first objective. The implementation of a simplified CC scheme is also being explored, which will permit us to go beyond MP2, at least for close-by pair excitations.

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