

Ground-State Properties of Crystalline Ice from Periodic Hartree-Fock Calculations and a Coupled-Cluster-Based Many-Body Decomposition of the Correlation Energy

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Ground state properties of crystalline ice *Ih* are investigated by combining periodic Hartree-Fock calculations with a many-body expansion for the electron correlation energy using second-order many-body perturbation theory and coupled-cluster techniques. Very good agreement with experimental data can already be achieved by considering two-body correlation contributions up to the third coordination shell in crystalline ice. This hints at the possibility to accurately simulate *ab initio* water by using periodic Hartree-Fock calculations together with a parametrized two-body correlation potential.

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Water and ice have been and still are subject to innumerable experimental and theoretical studies, due to their abundance on Earth and their important role in many chemical, biological, or geological processes, or simply because of their many unusual properties [1]. Understanding these properties is crucially linked to understanding the hydrogen bond network that forms in water's liquid and solid phase. The accurate quantum theoretical simulation of water is, however, still a formidable task.

Computationally, a multitude of quantum chemical methods are routinely used to study water clusters [2–4]; extended systems are usually investigated by (semi-) classical force field simulations or density-functional-theory (DFT) based calculations [5–7]. On the *ab initio* side, it is highly desirable to go beyond periodic Hartree-Fock (HF) calculations and include electron correlation for extended aqueous systems. However, the treatment of electron correlation from first-principle methods constitutes one of the most fundamental problems in solid-state physics, e.g., it is currently not known how to treat systems with small band gaps (e.g., metals) using accurate electron correlation methods such as coupled cluster, which are standard in molecular electronic structure theory [8,9].

A major improvement in this direction consists of the introduction of the incremental correlation method by Stoll and co-workers [10,11], which was successful even for metallic systems like mercury [12]. Note, however, that while this method is a way to systematically obtain correlation energy corrections, it is not a true two-particle theory that provides correlated wave functions in a periodic system. Recently, we showed that the electron correlation energy of small water clusters converges rapidly with the order of the many-body decomposition in the interaction energy, much faster than the total interaction energy [13]. While this illustrates the local nature of electron correlation, it also raises the question whether solid water could be described by combining periodic boundary condition HF calculations with localized correlation energy calculations

truncated at the two- or three-body level. If the former is sufficient, for instance liquid water could be simulated from *ab initio* wave-function-based methods by combining HF calculations and a parametrized dimer correlation potential, in the spirit of a recently presented *ab initio* water pair potential [14]. In this Letter, we show that ground state properties of crystalline ice can indeed be calculated very accurately by considering two-body correlation contributions on top of periodic HF calculations.

In the incremental approach the total interaction energy of ice is separated into a HF term E_{HF} and electron correlation term E_c :

$$E = E_{\text{HF}} + E_c. \quad (1)$$

E_{HF} is obtained from periodic HF calculations, whereas E_c for a N particle system is subjected to a many-body expansion [15]:

$$\begin{aligned} E_c(N) &= \sum_n E_c^{(n)}(N) \\ &= \sum_i E_c^{(1)}(i) + \sum_{i<j} E_c^{(2)}(ij) + \sum_{i<j<k} E_c^{(3)}(ijk) + \dots \end{aligned} \quad (2)$$

Exploitation of translational symmetry allows us to discard one summation index in the sums of (2) and also leads to faster convergence. If the series (2) converges sufficiently fast, it can be truncated after the two- or three-body terms $E_c^{(2)}(ij)$ or $E_c^{(3)}(ijk)$.

We simulate the most common crystalline phase of ice under ambient conditions, hexagonal ice *Ih*. Its hydrogen bond disorder is considered by using a dipole moment-free 16 molecule super cell [16]. HF total energy calculations are performed using the CRYSTAL06 [17] program package. Atom-centered Gaussian basis sets for these (periodic boundary) calculations have to be chosen carefully: too-diffuse basis functions cause linear dependencies or prohibit convergence of the self-consistency procedure, while

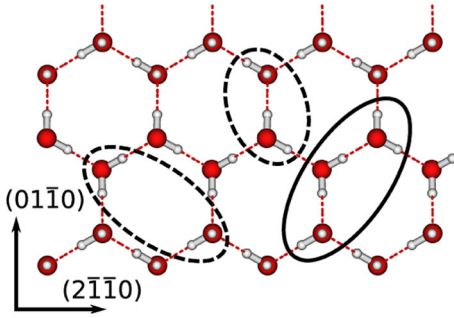


FIG. 1 (color online). Ice *Ih* crystal structure, depicting water dimers (dashed lines) and trimers (solid line), used in the two-body and three-body correlation calculations, respectively.

too-small basis sets fail to describe correctly the hydrogen bonds in ice and produce large basis-set superposition errors (BSSE) [18]. We found several oxygen basis sets previously used in periodic HF calculations [19,20] as well as common double- ζ basis sets [21,22] not to be suitable for describing ice. Dense, proton-ordered ice phases have been calculated successfully [23,24] using the Hartree-Fock optimized split-valence 6–31G** basis sets developed by Pople *et al.* [25]. In our work Pople’s 6–311G** basis sets [26] are used for both oxygen and hydrogen. The Brillouin zone was sampled using eight special k points [27]. To calculate the binding energy of ice, the BSSE in

TABLE I. Ground state properties of ice *Ih* from *ab initio* and DFT calculations, compared to experimental values: equilibrium lattice constants a_0 , lattice energies E_b , bulk moduli B_0 , and their derivatives $B' = dB/dp$. DFT results from Ref. [34]; GGA functionals used: PW91 [35], PBE [36].

	a_0 [Å]	E_b [eV]	B_0 [kbar]	B'
Experiment	4.497 ^a	−0.580 ^b	89.0 ^c	
(including ZPVE)		−0.490 ^b		
HF	4.735	−0.402	100.4	3.97
HF + MBPT2(1)	4.686	−0.401	111.6	5.14
HF + MBPT2(2, NN)	4.549	−0.530	142.9	5.03
HF + MBPT2(2, 2NN)	4.518	−0.556	148.5	5.06
HF + MBPT2(2, 3NN)	4.504	−0.568	151.4	5.12
HF + MBPT2(2, 5NN)	4.501	−0.571	150.4	4.97
(including ZPVE)	4.529	−0.470	135.4	5.27
HF + MBPT2(3)	4.509	−0.569	150.7	5.05
HF + CCSD(T)(1)	4.687	−0.401	107.9	5.43
HF + CCSD(T)(2, NN)	4.560	−0.529	141.3	5.44
HF + CCSD(T)(2, 2NN)	4.522	−0.560	148.3	5.40
HF + CCSD(T)(2, 3NN)	4.505	−0.574	153.3	5.68
HF + CCSD(T)(2, 5NN)	4.501	−0.577	152.4	5.54
(including ZPVE)	4.529	−0.476	135.9	5.78
DFT-LDA	4.157	−1.139	263.6	4.56
DFT-GGA (PW91)	4.418	−0.702	157.6	4.71
DFT-GGA (PBE)	4.424	−0.670	149.0	5.01

^aFrom Ref. [37]

^bFrom Ref. [38]

^cFrom Ref. [39]

our solid-state HF calculations is corrected for by using the Boys-Bernardi counterpoise scheme: water’s gas phase energy is calculated with basis sets on the positions of all surrounding water molecules. The supercell [16] is generated by *two* water molecules in the asymmetric unit. Their internal coordinates and the unit cell parameters are optimized over a range of fixed unit cell volumes V . The energy-volume curve $E(V)$ was fitted using Vinet’s equation of state [28].

Localized correlation calculations are performed using the MOLPRO [29] program package in conjunction with augmented correlation consistent triple- ζ basis sets [30]. Both second-order many-body perturbation theory [31] [MBPT2] and coupled-cluster theory [32,33] [CCSD(T), including single, double, and perturbative triple excitations] are used to calculate correlation energies. Figure 1 illustrates the two- and three-body terms studied here. Up to two-body next-nearest-neighbor interactions the system’s geometry is optimized with respect to the total energy $E = E_{\text{HF}} + E_c$. Correlation contributions from outer neighbor shells are added as single point energy corrections; all CCSD(T) energies are computed using the respective MBPT2 geometries.

Essential results of the HF (plus correlation) calculations are compiled in Table I and compared to experimental data. See also Figs. 2 and 3 for the correlation contributions to the total energy with varying lattice constant. The experimental lattice energy was obtained by Whalley by adjusting ice’s heat of sublimation for zero-point vibrational energy (ZPVE) corrections [38].

Pure HF calculations underestimate the hydrogen bond network, yielding too large a lattice constant and too-small a binding energy. Including one-body MBPT2-correlation

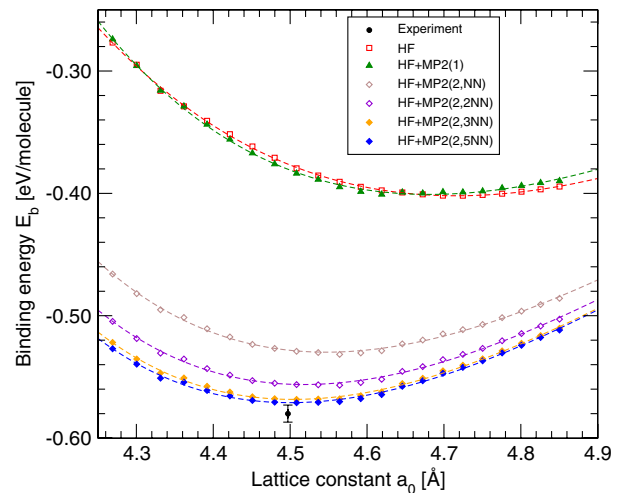


FIG. 2 (color online). Lattice energy of ice from HF calculations and various MBPT2 correlation treatments, compared to experiment [37,38]. Notation: MP2(2, x NN) denotes periodic HF calculations plus two-body MBPT2 up to the x th shell in nearest neighbors.

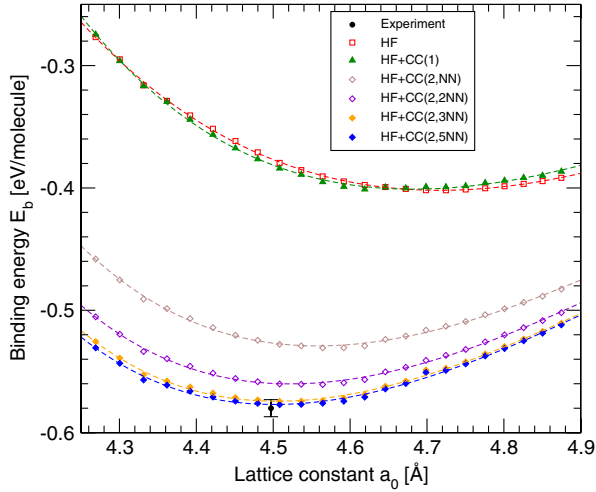


FIG. 3 (color online). Lattice energy of ice from HF calculations and various CCSD(T) correlation treatments, compared to experiment [37,38]. For notation see Fig. 2

terms $E_c^{(1)}(i)$, i.e., intramolecular correlation energies, does not improve these results. This is expected as most ground state properties depend on the correct description of the *inter*-molecular hydrogen bonds. However, including two-body terms $E_c^{(2)}(ij)$ leads to close agreement with experimental results, depending on the spatial extent over which the interactions are considered. Table I illustrates the improvement achieved by successively including outer neighbor shells into the two-body energy summation. We find the two-body interaction energy to be converged after including the third nearest-neighbor shell, that is, including the 30 closest dimer correlation contributions for every molecule in the unit cell, up to a distance of roughly 7 Å at equilibrium lattice constant. Including the 4th and 5th nearest neighbors (about 150 additional dimer terms, up to a distance of roughly 11 Å) sums up to very small energy contributions of about -2 to -5 meV per molecule. A similarly rapid convergence behavior was previously found in rare gas solid-state calculations [40]. The thus obtained lattice constants of 4.5006 Å [4.5010 Å] from MBPT2 [CCSD(T)] are in excellent agreement with the experimental result of 4.497 Å. The c/a ratio of 1.627 also agrees with experiment (1.628, [37]); at HF level, $c/a = 1.609$ is significantly smaller. Similarly, the lattice energy of -0.571 eV [-0.577 eV] per molecule is very close to the experimental value of -0.580 ± 0.007 eV per molecule. The experimental value for the bulk modulus was obtained at $T = -16$ °C and is thus significantly smaller than the calculated values of about 150 kbar at absolute zero. Extrapolating experimental fits for $B_0(T)$ to absolute zero yields values ranging from $B_0(0) = 107$ kbar [41] to $B_0(0) = 121$ kbar [39], still much smaller than the calculated value. We conclude, however, that for the two-body summation of the correlation energy, a cutoff radius of

about 7 Å gives reasonably converged results, and the bulk modulus calculated at the coupled-cluster level is the most reliable reference value at 0 K.

In water clusters, the three-body correlation energy $E_c^{(3)}(ijk)$ was previously found to be much smaller than the two-body term $E_c^{(2)}(ij)$ [13]. Moreover, that study found the three-body correlation to be mostly compensated by an equally large four-body term of opposite sign. For crystalline ice, the magnitude of the three-body correlation is estimated by considering the most important three-body terms: water trimers within the unit cell with *two* hydrogen bonds, i.e., the most closely arranged trimer configurations that can be constructed, cf. Fig. 1. Their contributions to the total energy sum up to between -0.4 and $+5$ meV per molecule over the lattice constant range considered; the changes in the ground state properties are small; see Table I. Three-body terms from more distantly located trimer configurations are expected to contribute much less to the correlation term $E_c^{(3)}(ijk)$. At equilibrium lattice constant, it holds $E_c^{(3)}(ijk) = 0.0012E_c^{(2)}(ij)$, confirming the rapid convergence of the many-body expansion already found in water clusters. Thus, it should be reasonable to truncate the expansion after the two-body term, which in turn can be spatially restricted to a maximum distance of about 7 Å between the molecules considered.

DFT calculations [34] give less accurate results. The local density approximation (LDA) for the electron exchange-correlation energy overestimates the hydrogen bond strength severely, resulting in a lattice constant 7.5% too small. Generalized-gradient-approximation (GGA) functionals give better crystal parameters and bulk moduli, but still overestimate the lattice energy by about 100 meV per molecule. Judging from the HF calculation's underestimation of the hydrogen bond strength, it is expected and has been found recently [42] that hybrid-density functionals (by mixing in some exact exchange) should be somewhat better suited to describe solid water or ice. The optimized effective potential method [43,44] is another promising option to go beyond DFT.

The ZPVE of ice has been estimated to be 90 meV per molecule from experimental vibrational data [38], and 88 meV per molecule from DFT calculations [34]. Here, we perform a similar analysis for our calculated *ab initio* structures. Lattice vibrations are calculated at MBPT2 level of theory, using an augmented double- ζ basis set [30], for the central molecule of a $(\text{H}_2\text{O})_5$ cluster embedded in the dipole electrostatic field of surrounding ice [45]. Acoustic (translational and librational) modes are occupied using the Debye model, optical (intramolecular) modes using the harmonic Einstein model. Over the volume range considered, energy shifts range from 110 to 87 meV per molecule, with 102 meV at the equilibrium lattice constant. The binding energy of -0.470 [-0.476] eV from MBPT2 [CCSD(T)] calculations compares well to the experimental heat of sublima-

tion of -0.490 eV; see Table I. However, the equilibrium lattice constants are about 0.7% higher than in experiment. The simple model employed here most likely overestimates the ZPVE corrections, and a more accurate treatment of the phonon dispersion or the inclusion of anharmonicity effects should yield better results. The corrected bulk moduli decrease to about 135 kbar, in better agreement with extrapolated experimental results.

In conclusion, we have presented the first *ab initio* many-body decomposition for the total energy of crystalline ice. In line with recent water cluster calculations it was shown that it is sufficient to truncate the correlation energy expansion after the two-body term. The calculated ground state properties agree very well with experimental data. We predict the bulk modulus of ice at very low temperatures to be higher than extrapolations from high-temperature measurements suggest. The fast convergence of the correlation energy (both in the many-body expansion and the spatial extent of the interaction) justifies the combination of periodic HF calculations with a parametrized high-level *ab initio* dimer correlation potential, for instance in liquid water simulations.

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