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Predicting lattice energy and structure of molecular crystals by first-principles method: Role of dispersive interactions

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ABSTRACT

The accurate calculation of lattice energy and structure of molecular crystals represent a test of the ability of first-principles periodic density functional method to model the relatively weak intermolecular interactions found in molecular crystals. The weak intermolecular dispersion interactions need to be considered for the accurate prediction of crystal structure and lattice energy of molecular crystals. In this paper, we report the calculation of lattice energies and structure of a set of eight molecular crystals at the *ab initio* level of theory. Hartree–Fock and density functional theory with and without dispersion correction potential were employed. Our results clearly show with application of triple zeta polarization (TZP) basis set, the lattice parameters obtained using B3LYP functional with dispersion interactions give better agreement with the experimental results. On the other hand, the lattice energies obtained using B3LYP-D/TZP method is severely underestimated. The lattice energies calculated at B3LYP-D/6-31G(d,p) level of theory are in close agreement with the corresponding experimental results because of smaller size of basis sets provide large basis set superposition errors which compensate the missing dispersion energies.

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1. Introduction

The structure and binding energy of molecular crystals play a central role in controlling the process parameters in the pharmaceutical and fine chemical industry. Their structures and particulate properties greatly affect the handing and processing of materials [1]. The accurate calculation of structure of molecular crystals presents a formidable challenge of contemporary interest. The forces between all the molecules during crystallization process determine the resulting crystal structure, but a priori crystal structure prediction remains a difficult task [2]. Crystal lattice energies are important in considering the stability of new materials [3]. The lattice energy reflects the natural tendency towards the organization of matter. Accurate determination of the lattice energies of molecular crystals has paramount importance in crystal engineering, which is crucial in many applications such as the development of pharmaceutical products and optical materials [4]. Periodic *ab initio* method is the most obvious technique to use, but it requires corrections for the dispersion interactions. Alternatively, second-order Møller–Plesset perturbation theory (MP2) captures the dispersive interactions naturally, and its local periodic implementation has become practical in recent years [5]. However, periodic MP2 calculations remains limited to unit cells with around 50 atoms in a medium-sized basis sets, and post-MP2 correlation effects can be important.

The empirical force-fields method is generally employed to calculate lattice energy of molecular crystals. Nevertheless, being an empirical method, force fields method has inherent limitations for providing reliable energy calculations, particularly for those structures that vary greatly from those used to develop the force field. However, modern force fields are not completely empirical methods and yield results that are comparable with the results obtained with quantum mechanical method. The molecular crystals have relatively smaller lattice energy which further poses a significant challenge to force fields method to predict different polymorphs. On the other hand, the quantum mechanical methods may be capable of producing precise energy calculations for the molecular crystals. However, difficulty arises in considering the long-range van der Waals (vdW) interaction [6, 7]. Hartree–Fock (HF) theory completely lacking such interactions. In contrast to this, the formulation of density functional theory (DFT) gives the exact description of ground state energy including vdW energy [8]. The practical implementation of DFT to account vdW energy relies on the approximation of exchange-correlation functional. Recently, it has been shown that hybrid exchange-correlation functional is quite successful in predicting structure and lattice energy of molecular crystals [9,10].

In this paper, we focus our attention on the calculations of lattice energy and structure of many molecular crystals namely, α-resorcinol, β-succinic acid, hexamine, α-RDX and several amino acid including (R, S)-alanine and α, β, γ polymorph of glycine

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crystals, within the framework of periodic Hartree–Fock and density functional theory using hybrid exchange-correlation functional. For this purpose, dispersion corrected and un-corrected interactions are employed to study the role of dispersion forces on the structures and lattice energies. Results are reported for the optimized lattice parameters and lattice energy of a set of eight organic crystals. A systematic comparison with experimental data has been carried out in order to access the accuracy of with and without dispersion corrected DFT and HF methods in determining structure and lattice energy.

2. Computational method

All the calculations of crystal structure and lattice energy of all molecular crystals considered in this study have been performed using CRYSTAL09 code [11], which is an *ab initio* program based on linear combination of atomic orbitals for the treatment of periodic systems. Crystalline orbitals are represented as linear combinations of Bloch functions and are evaluated over a regular three-dimensional mesh in reciprocal space. Each Bloch function is built from atom-centred atomic orbitals, which are contractions (linear combinations with constant coefficient) of Gaussian-type functions (GTF), each GTF being the product of a Gaussian times a real solid spherical harmonic. HF and DFT based *ab initio* approaches have been performed with B3LYP exchange-correlation functional (hereafter refereed as DFT-B3LYP). In order to take the effect of dispersive interactions DFT based calculations with B3LYP exchange-correlation functional augmented with empirical dispersion terms (B3LYP-D) as proposed by Grimme has been employed [12]. It has been widely demonstrated that the Hybrid functionals and, in particular, the B3LYP functional, give precise results for structure, energetic and vibrational properties of molecules and solids [9,10,13,14]. The results obtained using B3LYP functional are better than the one obtained with exchange-correlation functional within the local density approximation and generalized gradient approximation. We have tested three all-electron Gaussian basis sets, namely 6-21G and 6-31G(d, p) which are standard Pople's split-valance basis sets, and triple-zeta plus polarization (TZP) devised by Ahlrichs and co-workers to study the effect of basis set and dispersion forces on the lattice energy and structural parameters of the molecular crystals [15,16]. Civalleri et al. [10] showed that TZP basis set is quite effective to reduce basis set superposition error in calculations on molecular crystals. The shrinking factor of the reciprocal space net for each molecular crystal was used to define a mesh of points in the irreducible Brillouin zone in order to meet the convergence criteria [17].

In order to calculate Coulomb contributions to the total energy and Fock matrix, truncation criteria for the evaluation of infinite Coulomb and exchange series must be specified. It is based on the overlap between two atomic functions which depend on the geometry of a crystal. Apart from this, bipolar expansion is used to expand Coulomb and exchange integrals in order to efficiently evaluate the integrals. The total energy change due to the bipolar expansion approximation is not greater than 10^{-4} hartree per atom. The level of accuracy in evaluating the Coulomb and exchange series are controlled by five thresholds, for which values of 10^{-8}, 10^{-8}, 10^{-8}, 10^{-8}, and 10^{-16} are used [11]. The selection of the tolerance values is performed according to overlap-like criteria: when the overlap between two atomic orbitals is smaller than thresholds, the corresponding integral is disregarded or evaluated in a less precise way. Details of criteria for choosing the five tolerances are discussed elsewhere [11].

The exchange-correlation contribution is evaluated by numerical integration over the cell volume. The self-consistent-field-cycle (SCF) converges when the root mean square (RMS) of the change in the eigenvalues from two subsequent cycles is less than 10^{-8} hartree or the change in the absolute value of the total energy is less than 10^{-7} hartree.

In order to obtain the fully relaxed structure of bulk crystals, we choose experimental crystal structures as starting geometry, a full relaxation of both lattice parameters and atomic coordinates by means of analytical energy gradients is carried out [18]. The geometry optimization of crystal structures are performed by means of a quasi-Newton optimization algorithm. Gradients were evaluated each time the energy is computed and the second derivative matrix is updated by means of the Broyden–Fletcher–Goldfarb–Shanno algorithm. At each step, a one-dimensional minimization using a quadratic polynomial is carried out, followed by an *n*-dimensional search using the Hessian matrix. Geometry convergence is tested on the RMS and the absolute value of the largest component of the gradients and estimated displacements. The threshold for the maximum force, the RMS force, the maximum atomic displacement, and the RMS atomic displacement on all atoms have been set to 0.00045, 0.00030, 0.00180, and 0.00120 au, respectively. The symmetry of slices is maintained during the all surface relaxation calculations. In order to check whether the optimized structure has reached equilibrium geometry or not, a stationary point on the potential energy surface is found where the total force acting on atoms is numerically zero. Geometry optimization is usually completed when the gradients are below a given threshold. In CRYSTAL09 code, the optimization convergence is checked on the RMS and the absolute value of the largest component of both the gradients and the estimated displacements. The structural optimization is successfully completed when all the four conditions set by the above thresholds are simultaneously satisfied. The symmetry of the crystals was maintained during the optimization process.

An empirical correction term to include long-range dispersion interactions in DFT methods as proposed by Grimme has been implemented in CRYSTAL09 code [12]. It is a damped pairwise London-type term given by,

$$E_{disp} = -s_6 \sum_{ij} \sum_{g} \frac{C_6^{ij}}{R_{ij,g}^6} \left(\frac{1}{1+e^{-d(R_{ij,g}/R_{vwd}-1)}} \right) \quad (1)$$

which has been added to the computed *ab initio* DFT total energy and gradients at the B3LYP level of theory. The summation in the above equation is over all atom pairs and g lattice vectors with the exclusion of self-interaction ($i=j$) for $g=0$. C_6^{ij} is the dispersion coefficient and R_{ij} is the interatomic distances between atom i in the reference cell and j in the neighboring cell. R_{vdw} is the sum of the van der Waals radii and d is the steepness of the damping function. The values of C_6, R_{vdw} and d were taken from Ref. [12]. The scaling factor, s_6, depends on the adopted exchange-correlation functional ($s_6=1.05$ for B3LYP method in Ref. [12]). A cut-off distance of 25.0 Å was used to truncate the summation over lattice vectors to obtain accuracy of order 0.02 kJ mol^{-1} to calculate lattice energy. We have carried out total energy calculations and geometry optimizations with and without including the empirical dispersion correction in order to estimate the effect of dispersion forces on structure and lattice energy. It has been shown that the inclusion of dispersion forces is crucial to properly model the weak intermolecular interactions that play an important role in determining weakly bonded molecular structure.

Particular attention has been paid to correct the basis sets superposition error (BSSE) to the lattice energy of all molecular crystals considered in this study. This is necessary since in the present calculations Gaussian-type of finite basis sets are used. BSSE is a consequence of using incomplete basis sets, and stems from the fact that fragment A of a system can use basis functions

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