

Supporting Information: Seamless and Accurate Modeling of Organic Molecular Materials

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Supplementary Tables

Table SI-1: The mean absolute error (MAE), standard deviation (SD) and mean absolute relative error (MARE) of different vdW-inclusive DFT methods with respect to the CCSD(T) binding energies of the S66 \times 8 database. In the analysis the eight binding distances are given equal weight.

	MAE (kJ/mol)	SD (kJ/mol)	MARE (%)
Overall Performance (66)			
PBE+TS	1.54	1.66	13.6
PBE0+TS	1.40	1.61	11.2
PBE+MBD	1.09	1.54	9.8
PBE0+MBD	1.01	1.56	8.5
Hydrogen bonding (23)			
PBE+TS	1.56	1.30	6.06
PBE0+TS	1.58	1.57	5.18
PBE+MBD	1.25	1.34	4.56
PBE0+MBD	1.37	1.81	3.96
Dispersion bonding (23)			
PBE+TS	1.94	2.18	23.96
PBE0+TS	1.59	1.96	18.49
PBE+MBD	1.26	1.87	17.26
PBE0+MBD	1.03	1.45	15.31
Mixed/Other (20)			
PBE+TS	1.04	1.14	10.32
PBE0+TS	0.96	0.96	18.49
PBE+MBD	0.69	0.98	7.10
PBE0+MBD	0.58	0.80	5.93

Table SI-2: Experimental sublimation enthalpies (at 298 K), vibrational contributions, experimental lattice energies and DFT-predicted lattice energies of the X16 molecules. Experimental sublimation enthalpies are taken from Roza and Johnson,¹ except for that of anthracene.² All quantities are in kJ/mol.

	ΔH_{sub}^0	ΔE_{vib}	$E_{\text{latt,exp}}$	PBE+TS	PBE0+TS	PBE+MBD	PBE0+MBD
1,4-cyclohexanedione	81.1	-7.5	-88.6	-105.9	-101.2	-92.2	-88.2
Acetic acid	68.0	-4.9	-72.8	-82.6	-79.0	-78.3	-74.6
Adamantane	58.4	-11.0	-69.4	-108.0	-105.0	-81.0	-78.6
Ammonia	29.8	-7.4	-37.2	-45.4	-42.4	-42.9	-40.2
Anthracene	101.9	-10.8	-112.7	-134.4	-133.5	-121.8	-119.1
Benzene	45.1	-6.6	-51.7	-66.3	-62.0	-55.0	-51.0
Cyanamide	75.5	-4.2	-79.7	-94.3	-88.8	-94.3	-88.8
Cytosine	163.4	-6.4	-169.8	-172.6	-167.9	-170.0	-164.5
Ethylcarbamate	78.7	-7.6	-86.3	-99.2	-94.0	-92.1	-87.1
Formamide	71.8	-7.4	-79.2	-86.3	-84.0	-82.8	-82.0
Imidazole	81.4	-5.5	-86.8	-101.9	-96.3	-97.1	-91.4
Naphthalene	71.3	-10.5	-81.7	-99.9	-98.4	-87.4	-85.4
Oxalic acid (α)	93.7	-2.6	-96.3	-100.7	-98.5	-98.1	-95.7
Oxalic acid (β)	93.6	-2.4	-96.1	-104.3	-100.1	-98.6	-94.8
Uracil	129.2	-6.5	-135.7	-149.0	-144.6	-145.9	-140.4
Urea	93.8	-8.7	-102.5	-113.1	-111.4	-111.2	-109.7

Methodology: Pairwise and many-body dispersion methods

The Tkatchenko-Scheffler (TS) method³ uses the standard pairwise expression to recover the long-range dipole-dipole interaction energy:

$$E_{\text{disp}} = -\frac{1}{2} \sum_{ij}^N f_{\text{damp}}(R_{ij}) \frac{C_6}{R_{ij}^6} \quad (1)$$

Starting from a DFT electron density obtained by a semi-local functional, effective local volumes of atoms are defined based on Hirshfeld partitioning of the electron density.⁴ These volumes are then used to rescale free-atom C_6 values, which then represent atoms in a given local chemical environment. Coupling to DFT is achieved using a Fermi-type damping function, with the Hirshfeld volumes used to rescale free-atom vdW radii. A single fitted parameter is used to match the damping to individual functionals.

Full details of the many-body dispersion (MBD) method are given elsewhere.^{5,6} Briefly,

the method is a two stage process. In the first step each of the atoms is represented as a quantum harmonic oscillator (QHO) with a Gaussian width for each oscillator derived from the TS polarisabilities.^{5,7} The electrodynamic response of the resulting QHO system is obtained by direct inversion of the self-consistent screening matrix to obtain the so-called relay matrix.^{7,8} For a solid with N atoms in the unit cell, the screening matrix is $3N \times 3N$ in size. The periodic nature of solids was fully accounted for by including coupling terms in the screening matrix that represent interactions with periodic images of unit cell atoms. These terms were added within a spherical cut-off radius of ≈ 50 Å. Partial contraction of the relay matrix yields effective polarisability tensors for each atom in the unit cell. Using the single Páde approximation, screened frequency-dependent polarisabilities $\alpha^{\text{SCS}}(i\omega)$ can be determined.

In the second step, the MBD energy is calculated by numerical diagonalisation of the Hamiltonian representing the interaction of the N QHOs the atoms in the system are mapped onto:

$$H_{\text{MBD}} = -\frac{1}{2} \sum \nabla^2 \boldsymbol{\chi}_p + \frac{1}{2} \sum \omega_p^2 \boldsymbol{\chi}_p^2 + \sum_{p>q} \sqrt{\alpha_p \alpha_q} \omega_p \omega_q \boldsymbol{\chi}_p \mathbf{T}_{pq} \boldsymbol{\chi}_q, \quad (2)$$

where $\boldsymbol{\chi}_p = \sqrt{(\alpha_p \omega_p^2)^{-1}} \boldsymbol{\mu}_p$, α_p is the isotropised screened polarisability of the p^{th} atom obtained in the SCS step, ω_p is the screened static frequency and \mathbf{T}_{pq} is the dipole-dipole coupling tensor. The screened frequencies are obtained from the screened polarisabilities and C_6 values.^{3,5} The dipole-dipole coupling tensor is derived in the usual fashion from the Coulomb operator, which is range-separated to allow the MBD energy to match with a given DFT functional:

$$V_{\text{MBD}}(r_{pq}) = \frac{1 - \exp(-(\frac{r_{pq}}{R_{pq}^{\text{vdW}}})^\beta)}{r_{pq}}, \quad (3)$$

where $R_{pq}^{\text{vdW}} = R_p^{\text{vdW}} + R_q^{\text{vdW}}$ represents the correlation length of the MBD interaction, in terms of the vdW radii of the individual atoms. These radii are determined as $R_p^{\text{vdW}} = R_{0,p}^{\text{TS}} \left(\frac{\alpha_p^{\text{SCS}}}{\alpha_p^{\text{TS}}} \right)^{\frac{1}{3}}$ in a similar fashion to the TS vdW radii.³ The single free parameter in Eq. (3), β , is 2.56 for PBE and

2.53 for PBE0. To sample the reciprocal space of the dipole interactions the MBD Hamiltonian is solved for a supercell of $\approx 25 \text{ \AA}$ in each direction.

Methodology: Density functional theory calculations

For the molecular crystals database, DFT calculations were performed using the plane-wave code CASTEP (version 6.01).^{9,10} A plane-wave cut-off energy of 1000 eV was used for all calculations. For solid-state calculations a k -point sampling of at least 0.06 \AA^{-1} was used to sample reciprocal space. Isolated molecule calculations were carried out in supercells of at least 15 \AA in length, with a supercell of 20 \AA being employed for some of the larger molecules. Norm-conserving pseudo-potentials were employed for calculating lattice energies, while phonon calculations were performed using ultra-soft pseudo-potentials (with a consistently optimised geometry). Initial structures for the molecules were obtained from Ref.¹ and in the case of form-I aspirin from Cambridge Structural Database (CSD 195136).¹¹ The full geometries (lattice parameters and fractional coordinates) were optimised at the PBE+TS level. All subsequent calculations (*e.g.* MBD and PBE0) were performed on these PBE+TS geometries. Using finite-difference forces and stresses, PBE+MBD geometry optimisations have been performed for ammonia, urea and naphthalene. The changes in lattice parameters are of the order of 1–2%, with a smaller volume for naphthalene and urea and a marginally larger one for ammonia. Both the TS and MBD values are in good agreement with low-temperature neutron diffraction data and the use of the PBE+TS geometries for MBD and also PBE0 calculations is unlikely to have a significant impact on the results presented here. Further details of the PBE+MBD influence on geometries will be given elsewhere.

Phonon calculations (at the PBE+TS level) were used to estimate the vibrational contributions

to the enthalpy of sublimation using:

$$\begin{aligned} \Delta H_{\text{sub}}(T) = & - E_{\text{latt}} + (E_{\text{ZPE, gas}} - E_{\text{ZPE, solid}}) \\ & + \int_0^T \Delta C_p(T) dT + \sum \Delta H_{\text{trans}}, \end{aligned} \quad (4)$$

$$\Delta H_{\text{sub}}(T) = -E_{\text{latt}} + E_{\text{vib, gas}}(T) - E_{\text{vib, solid}}(T) + 4RT, \quad (5)$$

Care was taken to employ large enough supercells for the solid-state calculations so as to ensure that phonon dispersion was properly converged. Supercells of 9–10 Å in each direction were found to give good convergence, yielding larger vibrational contributions than unit-cell phonon calculations. This will be discussed further elsewhere. For naphthalene,¹² adamantane,¹³ anthracene¹⁴ and urea,¹⁵ experimental C_p data are available for the solid state and were used to obtain a semi-anharmonic vibrational contribution in conjunction with the DFT zero-point energies and isolated-molecule C_p values.

The calculations for the S66×8 database were performed using the FHI-aims code¹⁶ in the same manner as described elsewhere.^{5,6}

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