HM-IE: Quantum Chemical Hybrid Methods for Calculating Interaction Energies

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Accurate intermolecular potentials are needed for quantitative molecular simulations, but their calculation from quantum mechanics can be very demanding. We have developed several variations of a procedure, which we collectively refer to as quantum mechanical Hybrid Methods for Interaction Energies (HM-IE), to accurately estimate interaction energies from CCSD(T) calculations with a large basis set (LBS). HM-IE was tested for interaction energies of Ne_2, $(C_2H_2)_2$, and N_2−benzene for many orientations sampling the entire potential energy surface and was found to be in excellent agreement with the CCSD(T)/LBS results while requiring considerably less computational time and resources. Furthermore, for neon, an intermolecular potential fit to interaction energies using HM-IE and a potential fit to CCSD(T)/LBS energies resulted in nearly identical predictions for densities and vapor pressures.

Introduction

Molecular simulations have been used to predict a broad range of physical and thermodynamic properties, including protein-folding dynamics,[1−3] gas transport properties in nanostructures,[4−7] and phase behavior.[8,9] Quantum mechanics (QM) can be used to develop the intermolecular potentials (IP) necessary to accurately calculate properties from simulation. However, calculations of the interaction energies between molecules require approximations to the Hamiltonian and wave function. Dunning[10] investigated approximations such as HF, MP2, MP4, and CCSD(T) for various types of molecular interactions. In that work, the MP2 method was found to accurately predict measured binding energies for hydrogen-bonded systems and led to reasonable agreement for weakly bound molecules (interaction energies from a few kcal/mol to a fraction of a kcal/mol). However, only the CCSD(T) method resulted in an accurate representation of the binding energies for very weakly bounded systems (less than a tenth of a kcal/mol).[10] In addition, CCSD(T) is known to be required for accurate interactions in other systems, e.g., aromatic systems.[11] Moreover, these levels of accuracy were only achieved when a large basis set was used to accurately represent the electronic wave function, but the use of CCSD(T) with a large basis set (LBS) is computationally very demanding.

Hybrid or compound QM methods, such as the Gaussian-3 (G3) methods developed by Curtiss et al.[12,13] and those of Dunning and Peterson,[14] have been used to successfully estimate molecular properties by assuming that the separate effects of electron correlation and basis set size are additive. In the G3 methods, high level energy calculations, e.g., QCISD(T), are performed with small basis sets, and lower level calculations (MP2 and MP4) are performed with larger basis sets. These calculated results are then combined, resulting in accurate heats of formation, ionization potentials, electron affinities, and proton affinities to within ±8 kJ/mol with relatively fast calculations compared to QCISD(T) with large basis sets. Dunning and Peterson[14] also approximated the basis set dependence of CCSD(T) calculations with that of Møller−Plesset perturbation methods for various properties, e.g., dissociation energies, harmonic frequencies, and ionization potentials.[14] This method resulted in average absolute errors of less than 1.7 kJ/mol, 2 cm^{-1}, and 0.42 kJ/mol for dissociation energies, harmonic frequencies, and ionization potentials, respectively.

For interaction energies, several authors[15−18] have used MP2 to approximate the CCSD(T) energy at the basis set limit, i.e., the value from CCSD(T) with an infinitely sized basis set. This was done by calculating MP2 energies with several large basis sets, extrapolating to the basis set limit, and then combining this extrapolation with a CCSD(T) interaction energy calculated using only a small or moderately sized basis set. Similarly, for a small number of orientations and a single separation distance, Tsuzuki et al.[11] and Koch et al.[19] approximated CCSD(T)/LBS energies by calculating CCSD(T) with a smaller basis set and added to this result a correction based on the difference between MP2 energies with a LBS and a smaller basis set. However, this approximation for benzene−benzene interactions at CCSD(T)/aug(d)-6-311g* by Tsuzuki et al.[11] resulted in errors of 0.5−1.4 kJ/mol for the three orientations and the single separation distance they studied. In addition, an accurate approximation of the CCSD(T)/aug-cc-pVQZ interaction energies for benzene−argon studied by Koch et al.[19] still required the use of a reasonably large basis set (aug-cc-pVTZ) for the small basis set (SBS).

Presented here is a class of QM hybrid methods referred to as HM-IE (Hybrid Methods for Interaction Energies) that accurately approximates interaction energies calculated with CCSD(T) and a LBS, but requires considerably less computational time and resources. In HM-IE, an approach similar to that of the G3 methods,[12,13] Dunning and Peterson,[14] and others[11,15−19] is used, which assumes that the effects of electron correlation and basis set size are additive. However, unlike Tsuzuki et al.[11] and Koch et al.,[19] several hybrid methods to approximate CCSD(T)/LBS results were investigated for three different systems and a wide range of orientations and separation

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distances to verify the accuracy of these hybrid methods for various types of intermolecular interactions.

We stress that the goal of the method proposed here is not to approximate CCSD(T) results at the basis set limit, but rather to approximate results for CCSD(T) with a large, but finite basis set at a small fraction of the computational load. Of course, the results so obtained could then be used with other extrapolation methods to approximate the basis set limit results, as demonstrated for the neon dimer in this work.

Methods

All QM calculations were performed using the Gaussian 98[20] suite of programs. For some of the interaction energy calculations, a 3s2p1d basis set[21] of bond functions (bf) was placed at the center of mass (COM) between the molecules. Interaction energies were calculated as the difference between the energy of the molecular complex, E_{12}, and that of the individual molecules or atoms, E_1 and E_2

$$E^{\mathrm{int}} = E_{12} - E_1 - E_2 \tag{1}$$

A basis set superposition error (BSSE)[22] arises when calculating the interaction energy using eq 1 because the molecular complex contains more basis functions than that of the individual molecule(s). We reduced or removed the BSSE in all calculations by using the counterpoise correction method;[22] i.e., we calculated all energies using the full basis set of the dimer and bond function, if used.

HM-IE interaction energies, E^{int}[MPn:CC], are calculated as follows

$$\begin{aligned} E^{\mathrm{int}}[\mathrm{CCSD(T)/LBS}] &= E^{\mathrm{int}}[\mathrm{CCSD(T)/SBS}] + \\ &\quad (E^{\mathrm{int}}[\mathrm{CCSD(T)/LBS}] - E^{\mathrm{int}}[\mathrm{CCSD(T)/SBS}]) \\ &\cong E^{\mathrm{int}}[\mathrm{CCSD(T)/SBS}] + \\ &\quad (E^{\mathrm{int}}[\mathrm{MP}n/\mathrm{LBS}] - E^{\mathrm{int}}[\mathrm{MP}n/\mathrm{SBS}]) \equiv E^{\mathrm{int}}[\mathrm{MP}n{:}\mathrm{CC}] \end{aligned} \tag{2}$$

where MPn with $n = 2$, 3, or 4 is generic for MP2, MP3, and MP4(SDQ). (In this terminology, Tsuzuki et al.[11] and Koch et al.[19] used a method analogous to the MP2:CC method.) In addition, two combination hybrid methods, MPn/m:CC

$$E^{\mathrm{int}}[\mathrm{MP}n/m{:}\mathrm{CC}] = \frac{1}{2}(E^{\mathrm{int}}[\mathrm{MP}n{:}\mathrm{CC}] + E^{\mathrm{int}}[\mathrm{MP}m{:}\mathrm{CC}]) \tag{3}$$

were also considered where n/m is either 2/3 or 3/4, indicating MP2/MP3 and MP3/MP4(SDQ), respectively.

In HM-IE, the basis set contribution going from the CCSD(T)/SBS to the CCSD(T)/LBS level is approximated by the difference between the interaction energies at the MP2, MP3, or MP4 level with the same basis sets. Only two sets of energy calculations are required in eq 2: (1) the CCSD(T)/SBS calculation, which includes the MPn/SBS calculations, and (2) the MPn/LBS calculation. While the CCSD(T) method scales with the number of basis set functions, N_b, as N_b^7, MP2 and MP3 only scale as N_b^5 and N_b^6, respectively. Thus, the use of HM-IE can result in a significant reduction in the computational time for a given basis set.

Results and Discussion

Three distinct systems, Ne_2, $(C_2H_2)_2$ and N_2−benzene, were studied. These systems are small enough that CCSD(T)/LBS calculations can be done in a reasonable time to make a comparison with the HM-IE results in terms of accuracy and computational load. Also, for the systems considered, the interactions vary from purely dispersive to dispersive plus electrostatic interactions, and the LBS results will show that each system studied requires CCSD(T) calculations for accurate interaction energies. For the Ne_2 system, full electron correlation was included, while the frozen-core approximation was used for the two other systems.

TABLE 1: Absolute Average Deviations from the CCSD(T)/LBS Results in Units of kJ/mol with a ± Standard Deviation and Maximum Absolute Deviation (in Parentheses)[a]

	1. Ne_2	2. $(C_2H_2)_2$	3. $N_2-C_2H_6$
no. of points	25	142	17
	(A)		
MP2/LBS	0.14 ± 0.16 (0.59)	0.33 ± 0.31 (1.4)	3.6 ± 3.0 (11)
MP3/LBS	0.058 ± 0.049 (0.13)	0.11 ± 0.13 (0.73)	2.3 ± 1.8 (6.3)
MP4(SDQ)/LBS	0.076 ± 0.082 (0.29)	0.37 ± 0.35 (1.7)	1.7 ± 1.2 (4.3)
	(B)[b]		
MP2:CC	0.0046 ± 0.0088 (0.039)	0.026 ± 0.034 (0.21)	0.82 ± 0.55 (1.9)
MP3:CC	0.0054 ± 0.0054 (0.016)	0.017 ± 0.016 (0.061)	0.98 ± 0.66 (2.3)
MP4:CC	0.0053 ± 0.0034 (0.0090)	0.097 ± 0.10 (0.51)	0.87 ± 0.54 (2.0)
MP2/3:CC	0.0021 ± 0.0024 (0.012)	0.013 ± 0.016 (0.097)	0.085 ± 0.071 (0.23)
MP3/4:CC	0.0015 ± 0.0013 (0.0051)	0.041 ± 0.047 (0.23)	0.93 ± 0.59 (2.1)

[a] The SBS for systems 1, 2, and 3 is aug-cc-pVDZ+bf, aug-cc-pVDZ, and 6-31g(d), respectively. The LBS for systems 1, 2, and 3 is aug-cc-pVQZ+bf, aug-cc-VTZ, and 6-31+g(3d), respectively. [b] The results for the more accurate HM-IE methods appear in section B.

Neon Dimer. The Ne_2 system was investigated to determine if HM-IE can accurately represent the CCSD(T)/LBS energy for a system with very weak, purely dispersive interactions. This system is the least computationally intensive, but has the weakest interactions with a minimum interaction energy of only −0.334 kJ/mol obtained at the CCSD(T)/aug-cc-pVQZ+bf level. For the SBS, the aug-cc-pVDZ+bf basis set with 60 functions was used, and aug-cc-pVQZ+bf with 174 basis functions was used for the LBS. The 25 CCSD(T)/LBS interaction energies for Ne_2 in Table 1 were calculated at separation distances between 2.4 and 9.0 Å, and ranged from −0.334 to +3.9 kJ/mol. For this system, all five versions of HM-IE provide excellent results with a 1−2 order of magnitude improvement in accuracy over the MP2/LBS and MP3/LBS results (See Table 1).

Figure 1 contains a subset of the calculated Ne_2 interaction energies at separation distances near the potential minimum. We see that the energies from CCSD(T)/LBS and three versions of HM-IE are nearly indistinguishable (MP4:CC and MP3/4:CC are also indistinguishable, but were omitted from Figure 1 for clarity). In contrast, the MP2/LBS and MP3/LBS calculations produce markedly larger maximum absolute and average deviations. The largest deviations from the CCSD(T)/LBS energies for the hybrid methods are near the potential well and in the repulsive region of the IP. For the seven separation distances near the potential well, from 2.85 to 3.3 Å, MP2:CC, MP3:CC, MP2/3:CC, and MP3/4:CC result in absolute average deviations (AADs) of only 0.0015, 0.0068, 0.0026, and 0.0009 kJ/mol, respectively. The AAD of the MP2:CC method is slightly better than MP2/3:CC for these seven separation distances, though for all 25 Ne_2 interaction energies, MP3/4:CC is the most accurate.

To be successful, HM-IE requires the difference between MPn and CCSD(T) interaction energies using the SBS and LBS to

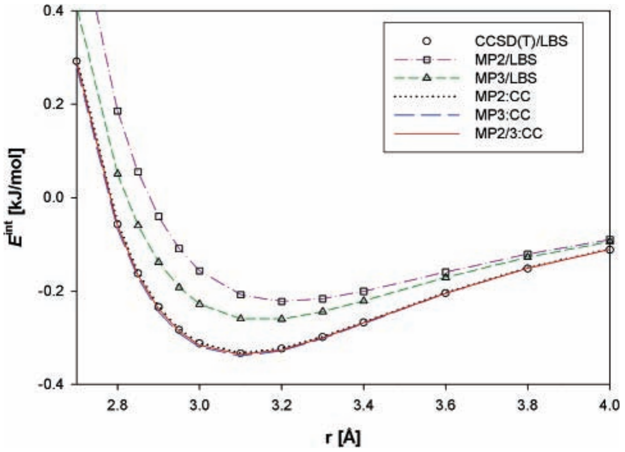

Figure 1. Interaction energies of Ne_2: LBS is aug-cc-pVQZ+bf and SBS is aug-cc-pVDZ+bf.

be approximately equal. The difference between MP*n* and CCSD(T) interaction energies for the aug-cc-pV*X*Z+bf basis sets, with *X* from 2 to 5, is nearly constant with respect to *X*. For example, with these four basis sets, the mean difference between MP2 and CCSD(T) is 0.1260 kJ/mol with a standard deviation of only 0.0018 kJ/mol. The standard deviations of the difference from CCSD(T) are 0.0028 and 0.0042 kJ/mol for MP3 and MP4(SDQ), respectively. Conversely, for the same four basis sets but without bond functions, the standard deviations are an order of magnitude higher, 0.027, 0.022, and 0.016 kJ/mol, for MP2, MP3, and MP4(SDQ), respectively. Similarly, we found that using a SBS of aug-cc-pVDZ without bond functions resulted in significantly worse predictions than using aug-cc-pVDZ+bf. For a separation distance of 3.1 Å, CCSD(T)/LBS predicts a binding energy of −0.334 kJ/mol, but MP2:CC, MP3:CC, and MP4:CC result in energies of −0.256, −0.278, and −0.294 kJ/mol, respectively, with aug-cc-pVDZ as the SBS. However, with a SBS of aug-cc-pVDZ+bf, MP2:CC, MP3:CC, and MP4:CC result in energies of −0.333, −0.339, and −0.326 kJ/mol, respectively. These results demonstrate that the basis set dependence of the difference between MP*n* and CCSD(T) energies is small, but even for the methods we are proposing, a SBS of sufficient size is required to accurately approximate the results for larger basis sets.

One important test of HM-IE is to determine how using an IP fit to interaction energies from HM-IE instead of energies from CCSD(T)/LBS affects the phase behavior predicted from molecular simulations. To study this, the CCSD(T)/LBS and MP2/3:CC interaction energies were fit to a C_6-Morse potential

$$U(r) = \epsilon[(1 - e^{-\alpha(r-r_{\min})})^2 - 1] + \left(1 - e^{d_6 r}\cdot\left[1 + \sum_{k=1}^{6}\frac{(d_6 r)^k}{k!}\right]\right)\frac{C_6}{r^6} \quad (4)$$

where r is the distance between the neon atoms. Knowing that an accurate representation of the long-range interactions is important for phase behavior predictions,[23] the asymptotic C_6 term was fit to interaction energies with separation distances between 6.0 and 9.0 Å. The remaining parameters were then fit to energies for separation distances between 2.6 and 9.0 Å by minimizing the root-mean-squared error. The parameter values and error for these fits can be found in Table 2, and we see that the C_6-Morse potential accurately fits both the CCSD(T)/LBS and the HM-IE interaction energies with similar parameters. The values of ϵ and $r_{\min}$ are sensitive to the small differences between CCSD(T)/LBS and MP2/3:CC interaction energies, but there is a correlation between these parameters: a larger $r_{\min}$ results in a smaller ϵ.

Gibbs Ensemble Monte Carlo (GEMC) simulations[24] were performed using these two potentials. *NVT* GEMC was used with the total number of particles *N* (512), total volume *V* of the two simulation boxes, and temperature *T* fixed. On average, each Monte Carlo cycle consisted of 512 attempted translations, one attempted volume change, and a sufficient number of particle exchange attempts to result in approximately one successful exchange. After a sufficient number of cycles for equilibration, production runs of 50 000−100 000 cycles were performed using periodic boundary conditions with a cutoff distance of one-half the box length. Standard long-range corrections to the energy and pressure were made, and various properties were averaged over the entire simulation.[25] The critical temperature and density were estimated from the simulation results using renormalization group theory and the law of rectilinear diameters.[25]

As shown in Figure 2a, the liquid and vapor densities calculated from the GEMC simulations are nearly identical for the two potentials with the MP2/3:CC-based potential resulting in only 0.54 and 2.2 mg/cm^3 AAD from CCSD(T)/LBS for the vapor and liquid densities, respectively. Also, there is only a 0.96% AAD difference in the vapor pressures predicted using the MP2/3:CC and CCSD(T)/LBS results, which is within the accuracy of the simulations (See Figure 2b.). As this study is concerned with efficiently obtaining accurate pair interaction energies, and since both quantum and multibody effects are known to be important for accurate predictions of noble gas-phase behavior from simulation but have been neglected here,[26,27] experimental densities and vapor pressures are not included in Figure 2. The goal here is only to show that the small differences in the pairwise intermolecular potentials obtained from the HM-IE and CCSD(T)/LBS calculations result in little difference in the predicted phase behavior.

Previous Ne_2 CCSD(T) calculations with a neon specific basis set of 240 basis functions, IO240,[28] resulted in a potential minimum (at 3.1 Å) of −0.3408 kJ/mol. With aug-cc-pVDZ+bf as the SBS and aug-cc-pVQZ+bf as the LBS, the MP2/3:CC method here results in a value of −0.3360 kJ/mol at 3.1 Å. However, if the LBS is increased to aug-cc-pV5Z+bf with 268 basis functions, the MP2/3:CC minimum value is −0.3409 kJ/mol, which deviates little from the previously reported result.[28] At a separation distance of 3.1 Å, fitting the CCSD(T) interaction energies for the aug-cc-pV*X*Z basis sets (*X* from 2 to 5) to an inverse power expansion in the maximum angular momentum, *X*, of the basis set[10]

$$E_{\mathrm{corr}}(X) = E_{\mathrm{a}} + \frac{E_{\mathrm{b}}}{X^3} + \frac{E_{\mathrm{c}}}{X^5} \quad (5)$$

results in a predicted basis limit value (E_{a}) of −0.3446 kJ/mol. (Basis sets without bond functions are used in the fit and extrapolation because the use of bond functions can result in behavior that is neither monotonic nor smooth with increasing basis set size.) Using eq 5 and the MP2/3:CC energies for the aug-cc-pV*X*Z basis sets (*X* from 3 to 5) with an SBS of aug-cc-pV(*X*−1)Z results in a basis set limit value of −0.3410 kJ/mol. The small difference between these two values demonstrates the accuracy of using HM-IE when approximating the basis set limit. Additionally, the basis set limit values differ only slightly from the value predicted using MP2/3:CC with a LBS of aug-cc-pV5Z+bf.

TABLE 2: C_6-Morse Potential Parameters for the Neon Dimer, Where the LBS Is Aug-cc-pVQZ+bf

	ϵ [kJ mol^{-1}]	α [Å^{-1}]	$r_{\min}$ [Å]	d_6 [Å^{-1}]	C_6 [kJ Å^6 mol^{-1}]	AAD [kJ mol^{-1}]
CCSD(T)/LBS	0.1451	2.307	3.218	2.100	90.40	2.8×10^{-4}
MP2/3:CC	0.1721	2.295	3.188	1.968	89.27	3.2×10^{-4}

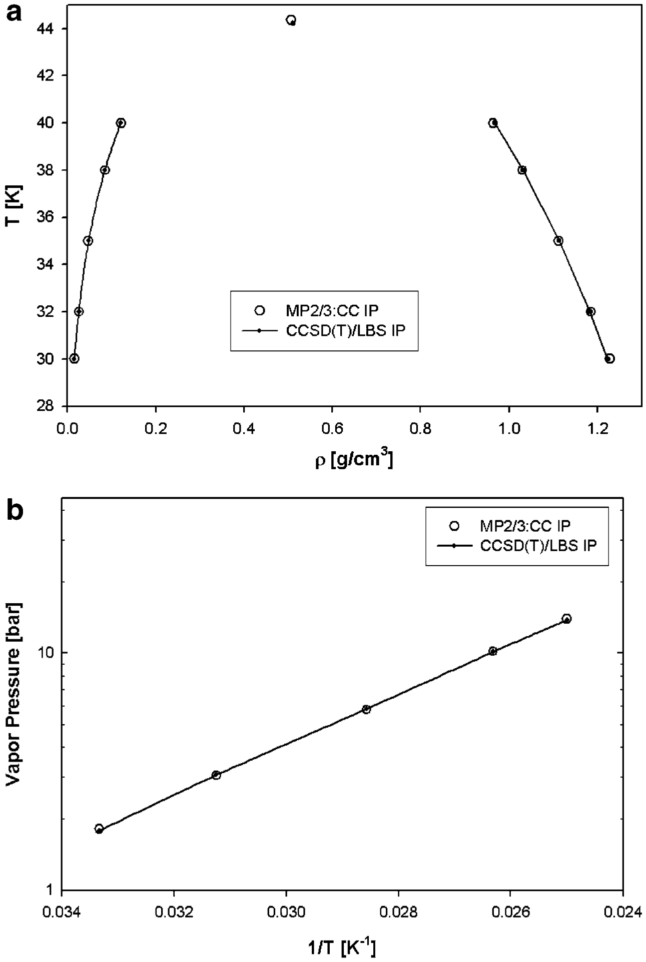

Figure 2. Saturated properties of neon from GEMC simulations: (a) vapor−liquid coexistence curves; (b) vapor pressure curves.

The calculation of one CCSD(T)/LBS counterpoise corrected interaction energy of Ne_2 in Table 1 requires 200 min on an AMD MP 1800+ processor. (All CPU times reported here are for this processor.) In contrast, the MP2:CC method requires only 26.5 min, and the MP3:CC, MP4:CC, MP2/3:CC, and MP3/4:CC methods require only 35 min. In addition, the MP2/3:CC-based IP results in nearly identical phase behavior predictions from GEMC simulations. Thus, for the Ne_2 system, HM-IE results in interaction energies accurate to within a few hundredths of a kJ/mol or less and nearly identical phase behavior compared to CCSD(T)/LBS while reducing the required CPU time by almost an order of magnitude.

Acetylene Dimer. The interactions between acetylene molecules, a combination of dispersion and weak electrostatic interactions, are stronger than those of neon and provide an another test of the HM-IE procedure. Although the small number of non-hydrogen atoms in the acetylene dimer would allow us to calculate the CCSD(T) interaction energies with relatively large basis sets in a reasonable amount of CPU time, disk limitations of Gaussian 98 on 32-bit, x86 computers limit the LBS to the aug-cc-pVTZ+bf basis set.

Several orientations were studied, of which three have a distinct symmetry: (1) a "T-shaped," π-type hydrogen-bonded orientation with C_{2v} symmetry; (2) a "slipped-parallel" orientation with C_{2h} symmetry with a 42° angle between the axis of the acetylene molecule and the line connecting the centers of mass (COM) of each monomer; (3) a "cross" orientation with D_{2d} symmetry in which the molecules are perpendicular to each other but out of plane. At certain COM separation distances, each of these orientations is a symmetry-constrained stationary point on the interaction energy surface. The C_{2v} structure is the minimum energy orientation, and the C_{2h} and D_{2d} structures are first- and second-order saddle points, respectively.[29] Twenty-five configurations at separation distances between 3.5 and 6.0 Å were studied for these three orientations. In addition to the symmetrical orientations, 27 pseudorandom orientations were generated using a shuffled Faure low discrepancy sequence as implemented in the IMSL C Math Library. Using these orientations, 117 configurations were constructed at separation distances between 4.0 and 6.0 Å. (In all cases, the bond length of acetylene was fixed at the equilibrium bond length, $R_{CH} = 1.062$ Å and $R_{CC} = 1.204$ Å.)[30] All 142 configurations were then used to investigate the ability of HM-IE to describe the entire potential energy landscape of the acetylene dimer.

For these calculations, the SBS was the aug-cc-pVDZ basis set with 128 basis functions, and the LBS was the aug-cc-pVTZ basis set with 286 basis functions. The CCSD(T)/LBS energies ranged from −6.0 to +3.6 kJ/mol for COM separations between 3.5 and 6.0 Å. MP2/3:CC resulted in the lowest AAD from the CCSD(T)/LBS energies for the T-shaped and slipped-parallel orientations with an AAD of 0.019 kJ/mol for the T-shaped configurations compared to AADs of 0.069, 0.045, 0.19, and 0.071 kJ/mol for the MP2:CC, MP3:CC, MP4:CC, and MP3/4:CC methods, respectively, and compared to AADs of 0.51, 0.060, and 0.69 kJ/mol for MP2/LBS, MP3/LBS, and MP4-(SDQ)/LBS, respectively. The improved accuracy of the HM-IE methods is not as apparent for the T-shaped configuration in Figure 3a as it is for the cross configurations shown in Figure 3b. In the cross orientation we see that both the MP2:CC and MP3:CC results are closer to the CCSD(T)/LBS energies than the MP*n*/LBS results, but both are slightly too attractive, which also then is the case for MP2/3:CC. For the cross orientation, all HM-IE methods better approximate the CCSD(T)/LBS results than any of the MP*n*/LBS methods except for MP4:CC, which is slightly less accurate than MP3/LBS, but more accurate than MP2/LBS and MP4/LBS. However, as seen in Table 1 for the 142 acetylene configurations studied, the maximum absolute and average absolute deviations for all five HM-IE methods are less than the deviations for the MP*n*/LBS methods, and MP2/3:CC is the most accurate overall with an AAD of only 0.013 kJ/mol.

In contrast to the neon results, MP4:CC has the largest overall AAD of the HM-IE methods, which is also reflected in the quality of the predictions from MP3/4:CC. For neon and acetylene, a few interaction energies were also calculated using MP4(SDTQ) in HM-IE instead of MP4(SDQ). The triples contribution was found to greatly improve the MP4:CC and MP3/4:CC predictions for acetylene and slightly improve the results for neon. The oscillatory nature of MP2:CC and MP3:CC for these two systems results in accurate MP2/3:CC predictions, but the oscillation between MP3:CC and MP4:CC results in accurate interaction energies with MP3/4:CC only when the triples contribution is included in the MP4 calculations.

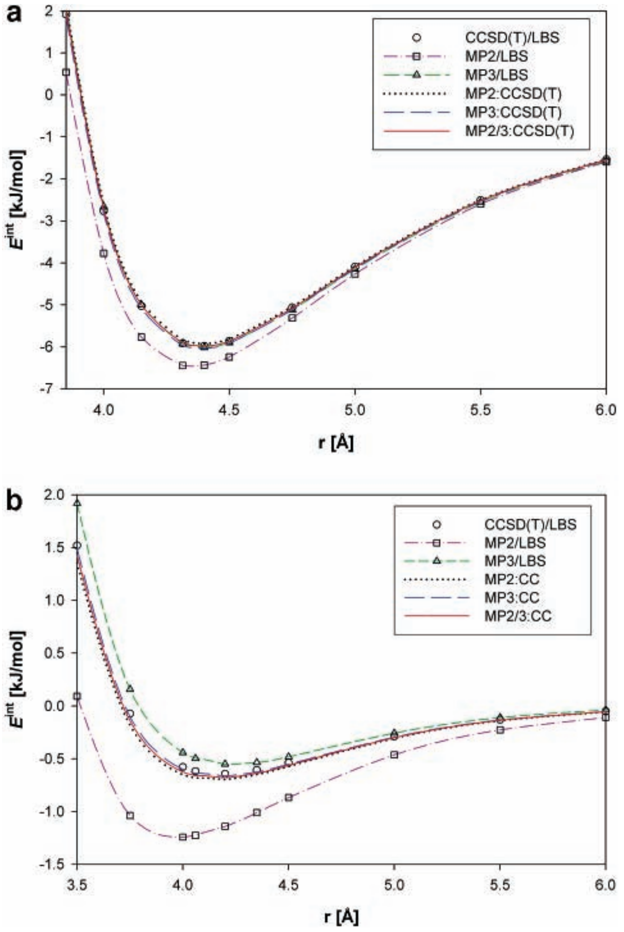

Figure 3. Interaction energies of $(C_2H_2)_2$ for various COM separation distances: LBS is aug-cc-pVTZ and SBS is aug-cc-pVDZ. (a) T-shaped orientation with C_{2v} symmetry; (b) cross-shaped orientation with D_{2d} symmetry.

However, including the triples contribution only results in a negligible reduction in computational load as a MP4(SDTQ)/LBS calculation is only marginally less expensive than a CCSD(T)/LBS calculation.

Most importantly, while a single counterpoise corrected CCSD(T)/LBS calculation requires 37 h without orbital symmetry, the MP2:CC, MP3:CC, and MP2/3:CC methods only require 5.5, 6, and 6 h of CPU time, respectively. (With symmetry the calculation times are reduced to 4, 5, 5, and 16 h for MP2:CC, MP3:CC, MP2/3:CC and CCSD(T)/LBS, respectively.) If a smaller SBS is used, for example the 6-31+g(d) basis set with only 80 basis functions, good but slightly less accurate results are obtained with AADs of 0.094, 0.080, and 0.050 kJ/mol for MP2:CC, MP3:CC, and MP2/3:CC, respectively. These results and those shown in Figure 4 again demonstrate that the accuracy of HM-IE improves as a larger SBS is used. Moreover, MP2/3:CC, with the 6-31+g(d) basis set as the SBS, has an overall maximum absolute deviation and AAD of 0.30 and 0.050 kJ/mol, respectively. These are less than half the deviations of MP3/LBS at the cost of only 11 additional minutes of CPU time, a 3% increase in computational time compared to the MP3/LBS calculation.

N_2−Benzene. The N_2−benzene system is the most computationally demanding of the systems considered here, as it contains eight non-hydrogen "heavy" atoms. In our calculations, the geometry of the benzene molecule[31] was fixed at $R_{CC} = 1.40$ Å, $R_{CH} = 1.10$ Å, and $\angle CCC = 120°$, and the bond length for nitrogen was fixed at 1.10 Å. Three orientations were studied, all with a 90° angle between the COM of nitrogen, the COM of benzene, and any carbon atom: (1) N_2 axis parallel to the C_6H_6 plane; (2) N_2 axis perpendicular to the C_6H_6 plane; (3) N_2 axis at 45° to the normal of the C_6H_6 plane. For these calculations, the 6-31+g(3d) basis set (260 basis functions) was chosen as the LBS as it accurately predicts the polarizability and quadrupole moment of the N_2, and the 6-31g(d) basis set (132 basis functions) was used for the SBS.

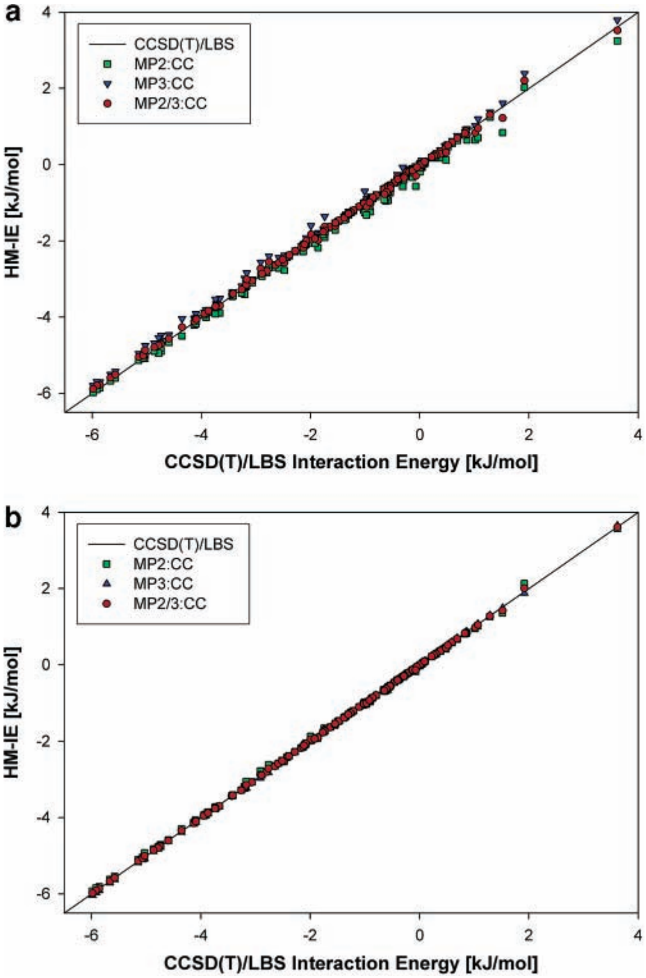

Figure 4. Interaction energies of $(C_2H_2)_2$ predicted from three versions of HM-IE. LBS is aug-cc-pVTZ. (a) SBS is 6-31+g(d); (b) SBS is aug-cc-pVDZ.

The CCSD(T)/LBS minimum energy in our calculations is −4.8 kJ/mol with a N_2 COM distance of 3.4 Å from the benzene COM and the N_2 axis parallel to the benzene plane. Shown in Figure 5 are the results of our QM calculations for nitrogen parallel to the benzene plane. (For clarity, the MP4(SDQ)/LBS results were omitted from Figure 5 since they closely match the MP3/LBS results.) The MP2/LBS binding energies are significantly more attractive than the CCSD(T)/LBS values with a maximum deviation of 5.5 kJ/mol for the points in Figure 5, while MP3/LBS overcorrects and results in interaction energies that are too repulsive by as much as 3.1 kJ/mol compared to the CCSD(T)/LBS results. MP2:CC, MP3:CC, and MP4:CC result in average deviations (not AADs) of only −0.59, +0.60, and +0.74 kJ/mol from the CCSD(T)/LBS results for the points shown in Figure 5. Both MP3:CC and MP4:CC result in interaction energy predictions that are less attractive than CCSD(T)/LBS, and therefore, MP3/4:CC also underpredicts the binding energies. As stated in the previous section, this is most likely the result of not including the triples contribution in MP4-(SDQ). Once more, in part because of the oscillatory nature of

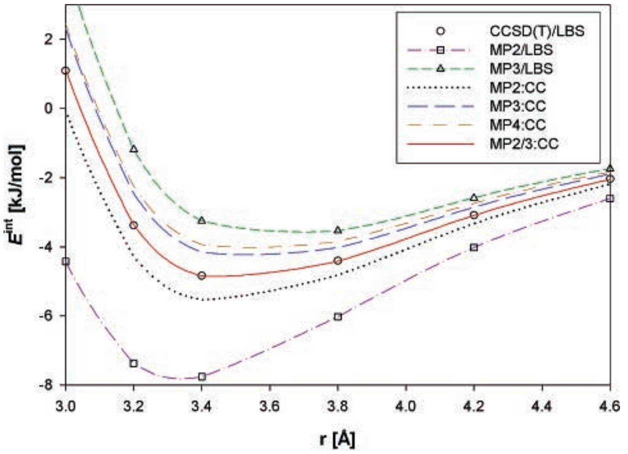

Figure 5. Interaction energies for various COM separation distances between N_2 and C_6H_6 with the N_2 axis parallel with C_6H_6 plane: LBS is 6-31+g(3d) and SBS is 6-31g(d).

the interaction energies in going from MP2:CC to MP3:CC, the MP2/3:CC energies are almost identical to the CCSD(T)/LBS results (AAD of 0.015 kJ/mol) as shown in Figure 5.

Similar results were obtained for the other nitrogen orientations, and the MP2/3:CC method resulted in the best approximation to the CCSD(T)/LBS results with an order of magnitude decrease in the AAD compared to traditional MP*n* methods, as seen in Table 1. Note that the AADs reported in Table 1 are for all 17 N_2–C_6H_6 interaction energies, for which the CCSD(T)/LBS energies ranged from −4.4 to +41 kJ/mol. The smallest errors are in the long-range part of the potential, which demonstrates that electron correlation is most important for the short-range and well regions of the potential.

In addition to improving the accuracy compared to MP*n*/LBS methods, the hybrid methods again significantly reduce the computational time compared to the CCSD(T)/LBS calculations. For CCSD(T)/LBS calculations, one N_2−benzene orientation requires 100 h of CPU time while the MP2:CC, MP3:CC, and MP2/3:CC calculations require only 3, 7, and 7 h of CPU time, respectively. Hence, for this system, MP2/3:CC provides an AAD in energies of approximately 0.1 kJ/mol compared to CCSD(T)/LBS but requires only 7% of the CPU time.

Conclusions

The results presented here demonstrate the accuracy and computational efficiency of the proposed HM-IE methods, especially the MP2/3:CC combination. As discussed for the Ne_2 and $(C_2H_2)_2$ systems, the choice of a SBS of sufficient size is important to accurately approximate the CCSD(T)/LBS energy. By using HM-IE, CPU time is significantly reduced compared to a CCSD(T)/LBS calculation, as is the disk space required to store the electron integrals, which otherwise may exceed the 16 GB limitation of Gaussian 98 on current 32-bit processors.

For the systems studied here, MP2/3:CC has an AAD from the CCSD(T)/LBS results of less than 0.1 kJ/mol, and is the best HM-IE method overall. However, all HM-IE methods result in more accurate approximations of the CCSD(T)/LBS energies than the MP*n*/LBS methods, but the general accuracy of MP3/4:CC requires the inclusion of the triples contribution in MP4. Thus, our results for these three distinctly different systems, which include rare gas molecules, aromatic molecules, and π-type hydrogen-bonded systems, demonstrate that HM-IE provides a means of quickly and efficiently calculating interaction energies that approximate the CCSD(T)/LBS results. Therefore, HM-IE is likely applicable to many systems and may allow for accurate interaction energies to be obtained for large systems that might not be possible to study at the CCSD(T)/LBS level.

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Note Added after ASAP Posting. This article was posted ASAP on 12/05/2003. Due to a production error, the column heading of column AAD [kJ/mol^{-1}] (column 7) in Table 2 was incorrect. It should have been AAD [kJ mol^{-1}]. The correct version was posted on 12/09/2003.

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