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Assessment and Validation of the Electrostatically Embedded Many-Body Expansion for Metal–Ligand Bonding

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Abstract: The electrostatically embedded many-body method has been very successful for calculating cohesive energies and relative conformational energies of clusters, and here we extend it to calculate bond breaking energies for metal–ligand bonds in inorganic coordination chemistry. We find that, on average, the electrostatically embedded pairwise additive method is able to predict bond energies yielded by conventional full-system calculations done at the same level of theory to within 2.5 kcal/mol and that the electrostatically embedded three-body method consistently yields energies within 1.0 kcal/mol of the full-system calculations.

An important theme of modern quantum chemistry is enabling reliable calculations on large and complex systems. A general strategy for achieving this is fragmentation, and a variety of fragmentation schemes have been explored.^{1–12} One especially promising approach is the electrostatically embedded many-body^{5,13–18} (EE-MB) expansion. In work reported so far, we have obtained accurate results at low cost for noncovalently bonded clusters. For example, the electrostatically embedded three-body (EE-3B) method based on CCSD(T) calculations of dimers and trimers was able to reproduce full water hexamer calculations with a mean unsigned deviation of only 0.12 kcal/mol (0.3%), whereas full CCSD calculations using the same basis set yielded a mean unsigned relative deviation of 0.43 kcal/mol (0.9%),¹⁴ and to reproduce full calculations on (H₂SO₄)-(HSO₄[−])(NH₄⁺)(H₂O)₆ with a mean unsigned deviation of only 0.15 kcal/mol (0.2%).¹⁷ In the present letter, we apply these methods to bond breaking energies of complexes bound by coordinate covalent¹⁹ bonds.

The EE-MB method is described elsewhere,⁵ and so it is reviewed only briefly here. The fragments into which the system is partitioned are called monomers. We will test two variants: the electrostatically embedded pairwise additive (EE-PA) method and the EE-3B method. In EE-PA, the energy of systems composed of monomers m , n , p , etc. is approximated as

$$E^{\text{PA}} = E^{(1)} + \Delta E^{(2)} \quad (1)$$

where

$$E^{(1)} = \sum_m E_m \quad (2)$$

$$\Delta E^{(2)} = \sum_m \sum_{n>m} \Delta E_{mn}^{(2)} \quad (3)$$

$$\Delta E_{mn}^{(2)} = E_{mn} - E_m - E_n \quad (4)$$

and the EE-3B energy is

$$E^{3\text{B}} = E^{\text{PA}} + \Delta E^{(3)} \quad (5)$$

where

$$\Delta E^{(3)} = \sum_m \sum_{n>m} \sum_{p>n} \Delta E_{mnp} \quad (6)$$

$$\Delta E_{mnp} = E_{mnp} - E_{mnp}^{\text{PA}} \quad (7)$$

where E_m , E_{mn} , and E_{mnp} are the energies of a monomer, dimer, and trimer, respectively, each embedded in a field of point charges representing the other monomers, and E_{mnp}^{PA} is the EE-PA approximation to the energy of trimer mnp . The individual embedded oligomer energies (where oligomer is a general term that can be replaced by monomer, dimer, or trimer) can be computed using any desired level of electronic structure theory. Most levels of electronic structure theory require that any system on which they are used have an integer number of electrons; therefore, charge transfer between oligomers of a given type usually cannot occur within most practical applications of the EE-MB approximation (including the present study).

All calculations were carried out with the M05-2X density functional²⁰ and the B2 basis set,²¹ which is a polarized valence triple- ζ basis set optimized for use with Zn-containing complexes. The innermost 10 electrons (small core) of Zn are replaced by the (MEFIT, R) relativistic effective core potential.^{22,23} The M05-2X density functional was chosen because of previous tests^{21,24} that showed it to yield high accuracy results for Zn-containing complexes and biological structures.

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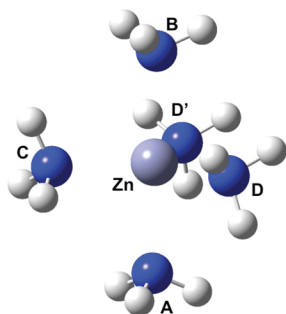


Figure 1. Structure of $\text{Zn}(\text{NH}_3)_5^{2+}$.

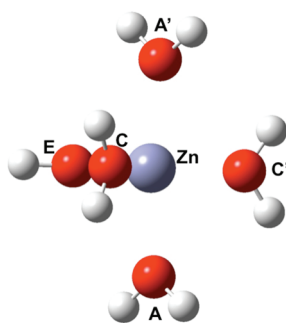


Figure 2. Structure of $\text{Zn}(\text{H}_2\text{O})_5^{2+}$.

All conventional calculations were performed using *Gaussian 09*.²⁵ All EE-MB calculations were performed using MBPAC 2009-2,²⁶ which is a program that requires the user to define which atoms in the overall system belong to each monomer and then calls MN-GFM,²⁷ a locally modified version of *Gaussian 03*²⁸ to perform the necessary monomer, dimer, and trimer calculations.

No attempt was made to correct for basis set superposition error (BSSE)^{29,30} in any of the present calculations for the following reasons: (1) The goal of this work is not to obtain high-level benchmark calculations of the binding energies of coordinate covalent clusters; rather, the goal of this work is to show that the EE-MB method can yield metal–ligand binding energies close to those of conventional calculations performed at a given level of theory. Therefore, attempting to correct for BSSE in the present study would be somewhat superfluous because it is not necessary in order to achieve our goal. (2) The counterpoise correction (CP)²⁹ for BSSE is only clearly defined for dimer interactions. Rigorous extensions of the CP correction for BSSE in trimer interactions and beyond have been proposed,³¹ but these methods are computationally costly. Rather than investing computer time in applying a many-body extension of the CP correction, one can invest that computer time (or less) into performing a non-BSSE-corrected calculation with a basis set large enough to preclude the need for such corrections. Often, a triple- ζ basis set with a judicious choice of polarization and diffuse functions will suffice.³²

The systems that we consider are (1) $\text{Zn}(\text{NH}_3)_5^{2+}$ (shown in Figure 1), (2) $\text{Zn}(\text{H}_2\text{O})_5^{2+}$ (Figure 2), and (3) $\text{Zn}(\text{H}_2\text{O})_4(\text{OH})^+$ (Figure 3). The quantities we calculate are bond breaking energies defined as the energy to remove one of the ligands from the complex, with the internal coordinates of both fragments frozen; thus, the quantity calculated here is not a conventional bond dissociation energy but rather a relative energy along a cut through the potential energy surface with

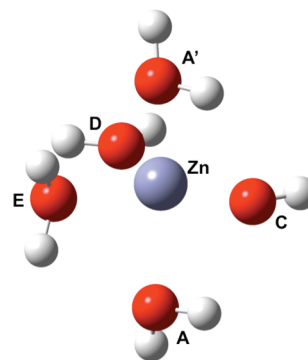


Figure 3. Structure of $\text{Zn}(\text{H}_2\text{O})_4(\text{OH})^+$.

fixed fragment geometries. This provides a direct test of the ability of EE-MB to predict relative electronic energies along bond breaking coordinates, with no complications from competing effects of relaxation. The energy of breaking the bond is the sum of the energies of the two products (separated frozen fragments) minus the energy of the reactant. When calculating the energies of a product, the embedding charges of the other (separated) product are not present because the other product is infinitely separated.

The geometries of the three complexes were optimized with M05-2X/B2/(MEFIT,*R*). Each of the coordination complexes has the structure of an irregular trigonal bipyramid, with axial ligands A and B and equatorial ligands C, D, and E. If r_X denotes the distance from the nonhydrogenic atom of a ligand to Zn, we label the atoms so that $r_A \leq r_B$ and $r_C \leq r_D \leq r_E$. Furthermore, if $r_B = r_A$, then B is also called A'; if $r_D = r_C$, then D is also called C', and if $r_E = r_D$, then E is also called D'.

The partial atomic charges on the fragments are calculated in every case for the isolated fragment at the geometry it has in the entire system. For example, if we are calculating the energy of ZnABCDE, and if one of the fragments is ZnCD, we calculate the partial atomic charges of ZnCD by removing A, B, and E from the system, and if another fragment is E, we calculate its partial charges by removing Zn, A, B, C, and D. Thus, the calculations used to obtain charges are the same as the monomer calculations of eq 2 except that, for obtaining charges, the monomers are not embedded. We do not want the results to depend strongly on the method used to calculate charges, and therefore we used three different methods to calculate charges in order to test the sensitivity. The methods used are Hirshfeld population analysis (HPA),³³ natural population analysis (NPA),³⁴ and Merz–Kollman (MK) electrostatic fitting.³⁵

For each of the three complexes, we considered two dissociation processes:



and



where n is 2 (Figures 1 and 2) or 1 (Figure 3). Notice that process R1 breaks an equatorial bond, and process R2 breaks an axial bond.

In preliminary work, we found that taking an isolated Zn^{2+} or a metal ion with a single ligand as a fragment did not yield accurate results; this is understandable because the Hirshfeld

Table 1. Target Bond Energies (kcal/mol)

process	complex	broken bond	bond energy
1	1	Zn–A	34.90
2	1	Zn–D'	45.97
1	2	Zn–A	40.06
2	2	Zn–E	45.68
1	3	Zn–A	25.22
2	3	Zn–E	33.23

Table 2. Unsigned Errors in Bond Energies (kcal/mol)

process	EE-PA			EE-3B		
	HPA	NPA	MK	HPA	NPA	MK
1	0.10	0.59	0.75	0.78	0.14	0.20
2	2.06	3.06	2.60	0.79	0.15	0.22
3	2.21	2.27	2.04	0.65	0.91	0.81
4	3.10	2.35	2.34	0.65	0.91	0.81
5	1.80	2.24	1.98	0.09	0.44	0.26
6	2.95	2.63	2.58	0.08	0.45	0.27
mean ^a	2.04	2.19	2.05	0.51	0.50	0.42

^a Mean unsigned error in all six cases.

partial atom charges of Zn in Zn^{2+} , $\text{Zn}(\text{H}_2\text{O})^{2+}$, and $\text{Zn}(\text{NH}_3)^{2+}$, at typical geometries in the latter two cases, are 2, 1.6, and 1.4, respectively, whereas in the larger fragments, the Hirshfeld partial atomic charge on Zn is much lower, in the range 0.5–1.2. Thus, we only consider fragmentation schemes where one of the fragments is Zn^{2+} with two ligands. In particular, because $r_{\text{equatorial}} < r_{\text{axial}}$, we take one fragment as ZnCD^{2+} for Figures 1 and 2 and ZnCD^+ for Figure 3. Note that A and B are NH_3 in Figure 1, they are H_2O in Figure 2, and A is OH^- and B is H_2O in Figure 3. We do not break the bond within the fragment because that gives a product where Zn has only one ligand in the fragment. In all cases, one fragment is Zn with the two closest ligands (which are always equatorial ligands), and the other fragments are individual ligands. We then consider breaking the bond between Zn and the farthest equatorial ligand or the bond between Zn and the nearest axial ligand.

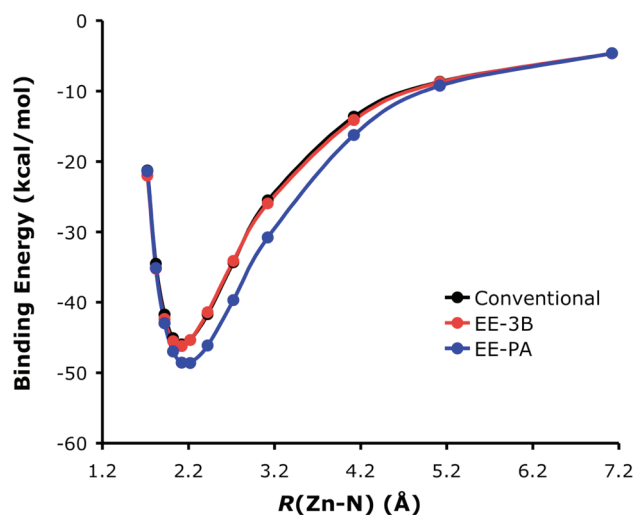
Our goal is to test how well the EE-MB approximation can reproduce a result on the whole complex. Therefore we first performed M05-2X/B2/(MEFIT,*R*) calculations on bond breaking without using the many-body approximation; the results are in Table 1. The table shows that the bond breaking energies vary by more than 20 kcal/mol for the various test cases. If we can predict the bond energies within 1 kcal/mol, we will have captured the variation within 5%. Table 2 shows the results. EE-PA has a mean unsigned error of about 2 kcal/mol, whereas EE-3B has a mean unsigned error of 0.4–0.5 kcal/mol, with a maximum error of 0.9 kcal/mol. So we judge the EE-3B theory to be a success for near-equilibrium structures.

In order to show that the EE-PA and EE-3B approximations also yield consistent performance on higher-energy, nonequilibrium structures, we selected several points along a slice of the potential energy surface (PES) of the $[\text{Zn}(\text{NH}_3)_5]^{2+}$ system shown in Figure 1. We adjusted the distance between Zn and the nitrogen atom of ammonia molecule D', holding the remaining $[\text{Zn}(\text{NH}_3)_4]^{2+}$ complex (composed of Zn²⁺, A, B, C, and D) and the D' ammonia molecule rigid in the geometries that they had in the $[\text{Zn}(\text{NH}_3)_5]^{2+}$ complex. At each Zn–N distance ($R(\text{Zn–N})$), we calculated the conventional, EE-PA, and EE-3B M05-2X/B2/(MEFIT,*R*) energies of the system. The

Table 3. Conventional Binding Energies (BE) and Errors in EE-PA and EE-3B Binding Energies As a Function of $R(\text{Zn–N})$ (All Values in kcal/mol)

$R(\text{Zn–N})$ (Å)	conventional BE (kcal/mol)	EE-PA error (kcal/mol)	EE-3B error (kcal/mol)
1.721	–21.26	–0.10	–0.75
1.821	–34.51	–0.61	–0.72
1.921	–41.73	–1.23	–0.61
2.021	–45.08	–1.90	–0.43
2.121 ^a	–45.97	–2.60	–0.22
2.221	–45.34	–3.27	–0.01
2.421	–41.68	–4.43	0.27
2.721	–34.32	–5.37	0.20
3.121	–25.52	–5.28	–0.43
4.121	–13.63	–2.61	–0.47
5.121	–8.66	–0.58	–0.09
7.121	–4.63	0.02	–0.01
MSE ^b		–2.33	–0.27
MUE ^b		2.33	0.35
RMSE ^b		2.98	0.43

^a This is the equilibrium geometry of the complex. ^b MSE = mean signed error, MUE = mean unsigned error, RMSE = root mean squared error.

**Figure 4.** $\text{Zn}(\text{NH}_3)_5^{2+}$ binding energy (in kcal/mol) as a function of the distance between zinc and the nitrogen atom of the ammonia molecule D' ($R(\text{Zn–N})$, in Å).

MK charges of the isolated rigid monomers ZnCD^{2+} , A, B, and D' were used as the embedding charges in the EE-MB calculations. Table 3 shows the conventional binding energy and the signed errors in the EE-PA and EE-3B binding energies (relative to the conventional energies) at each $R(\text{Zn–N})$. Figure 4 shows the actual binding energies calculated at each point on the PES slice using the conventional, EE-PA, and EE-3B methods. We again find that EE-PA has a mean unsigned error of about 2 kcal/mol and that EE-3B has a mean unsigned error of less than 0.4 kcal/mol. Therefore, we conclude that the EE-3B method is a success for a variety of metal–ligand complex geometries.

The present study shows that the EE-3B method consistently yields bond energies within 1 kcal/mol of those obtained from the full calculation at a given level of electronic structure theory. This is encouraging because using the EE-3B method instead of a conventional calculation is advantageous for the following reasons: (a) An EE-MB calculation at any level of electronic structure theory can easily be made to run on several processors

at once in order to save wall clock time. (b) A series of small calculations is less likely to exceed the memory or disk capacity of a computer system than is a single large calculation. (c) For systems with a large number of fragments (e.g., a coordinate complex in explicit solvent), an EE-3B calculation scales more favorably with the size of a chemical system than do conventional calculations at a high level of electronic structure theory (i.e., hybrid density functional theory or correlated wave function theory).

Previous studies (cited earlier) have shown that the EE-3B method is consistently able to predict binding energies of noncovalently bonded systems to within 1 kcal/mol (and often much less) of a conventional full-system calculation performed at the same level of theory. The complexes examined in those studies were held together by hydrogen bonds, intermonomer dispersion-like interactions, and electrostatic interactions between oppositely charged ions. The present study has examined systems held together by a stronger type of interaction: the coordinate covalent bond. We found that the EE-3B method consistently yields unsigned errors of less than 1 kcal/mol (relative to conventional calculations performed at the same level of theory) in the bond breaking energies of six bond breaking processes in three different zinc-ligand complexes when the zinc ion and the two ligands closest to it are treated as a single monomer. Consistent with previous studies, the errors in the EE-3B method do not depend strongly on the charge analysis method used to obtain the embedding charges; the EE-3B method performs well regardless of which set of embedding charges is used. We conclude that the EE-3B method is a convenient and accurate way to study relative electronic energies, i.e., potential energy surfaces, along bond breaking coordinates in coordinate covalent complexes.

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