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An Application of the Functional Boys-Bernardi Counterpoise Method to Molecular Potential Surfaces

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The "functional" counterpoise method, proposed by Boys and Bernardi [1], is applied to the theoretical prediction of hydrogen bonding potential surfaces, using a minimal basis to represent the atomic orbitals (STO-3G). Using this method, with a systematically chosen "correction factor", one can compute potential surfaces with an STO-3G basis as accurately as with a much more flexible atomic basis.

Die „funktionale" Ausgleichsmethode, von Boys and Bernardi [1] vorgeschlagen, wird zur theoretischen Vorhersage der Potentialflächen von Wasserstoff-Bindungen benutzt. Dabei werden die Atomorbitale durch einen minimalen Basissatz (STO-3G) dargestellt. Indem man diese Methode mit einem systematisch ausgewählten „Korrekturfaktor" benutzt, kann man Potentialflächen mit einer STO-3G Basis ebenso gut wie sonst nur mit einem sehr viel flexibleren Atombasissatz berechnen.

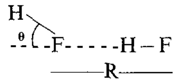
Introduction

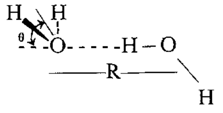
One of the important problems in molecular orbital potential surface calculations is the basis set choice; for most systems of chemical interest, one must use a relatively, small contracted gaussian basis. For small H-bonded complexes, the energies of dimerization found using an exhaustive basis set (with polarization functions) are in good agreement with available experimental data. The next level of basis set choice, a "double-zeta" representation of the atomic valence shells, exaggerates H-bond energies because it substantially overestimates the monomer dipole moments. Finally, small contracted *ab initio* bases (such as the STO-3G used here) predict a dimerization energy in better agreement with the "most accurate" calculations than the "double-zeta"; the STO-3G also predicts a greater dimerization energy than the "most accurate" (for $(H_2O)_2$, ΔE (most accurate) $= 4.7$ kcal/mole, ΔE (double zeta) $= 7.9$ kcal/mole ΔE (STO or STO-4G) $= 6.4$ kcal/mole) [2], despite the fact that the STO-3G predicted water dipole moment (1.8 D) is in excellent agreement with experiment, in contrast to the "most accurate" ($\mu = 2.1$ D).

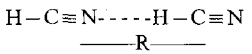
In the present work we rationalize why the STO-3G dimerization energy is larger than that found with the "most accurate" basis set and attempt to improve the STO-3G [3] computed potential curve by applying the so-called "functional counterpoise method" originally suggested by Boys and Bernardi [1].

Description of Calculations

The potential surface of the following hydrogen bonded systems was studied:







The energies for each geometry were computed by the well documented Roothaan SCF procedure for closed shell systems [4]. In the counterpoise method, the dimer energies E_{12} are computed in the usual way, but the monomer energies E_1 and E_2 are evaluated for each geometry point by using the full set of expansion

Table 1. All energies are in a.u.

$(HF)_2$ $E_0 = -98.57060$

R(a.u.)	θ	E dimer (a.u.)	E_1 + basis func. (2)	ΔE^a	$\Delta\varepsilon^b$	$\Delta\varepsilon + 1/6\,\Delta\varepsilon$
4.5	0	−197.14232	−98.58307	−0.0011	0.0125	0.0010
5.0	0	−197.14656	−98.57754	−0.0054	0.0069	−0.0044
5.5	0	−197.14548	−98.57374	−0.0042	0.0031	−0.0038
6.0	0	−197.14413	−98.57183	−0.0029	0.0012	−0.0027
6.5	0	−197.14332	−98.57107	−0.0021	0.0004	−0.0021
5.0	60	−197.14968	−98.58095	−0.0085	0.0104	−0.0068

$(H_2O)_2$ $E_0 = -74.96177$ a.u.

R(a.u.)	θ	E dimer, (a.u.)	E_1 + basis func. (2)	ΔE^a	$\Delta\varepsilon^b$	$\Delta\varepsilon + 2/7\,\Delta\varepsilon$
4.75	54	−149.93217	−74.97735	−0.0087	0.0156	−0.0042
5.25	54	−149.93396	−74.97094	−0.0105	0.0092	−0.0079
5.75	54	−149.93120	−74.96631	−0.0077	0.0045	−0.0064
6.25	54	−149.92858	−74.96371	−0.0050	0.0019	−0.0050
5.25	39	−149.933897	−74.97047	−0.0104	0.0087	−0.0079
5.25	0	−149.932995	−74.96966	−0.0095	0.0079	−0.0072

$(HCN)_2$ $E_0 = -91.67527$ a.u.

R(a.u.)	E dimer	E_1 + basis func. (2)	ΔE^a	$\Delta\varepsilon^b$	$\Delta\varepsilon + 4/11\,\Delta\varepsilon$
5.1	−183.34595	−91.68015	0.0047	0.0049	0.0064
5.67	−183.35564	−91.67847	−0.0050	0.0032	−0.0039
6.24	−183.35634	−91.67701	−0.0057	0.0017	−0.0051
6.68	−183.35522	−91.67606	−0.0046	0.0008	−0.0043

[a] E dimer $- 2E_0$.

[b] $E_0 - (E_1 + \text{basis func. (2)})$.

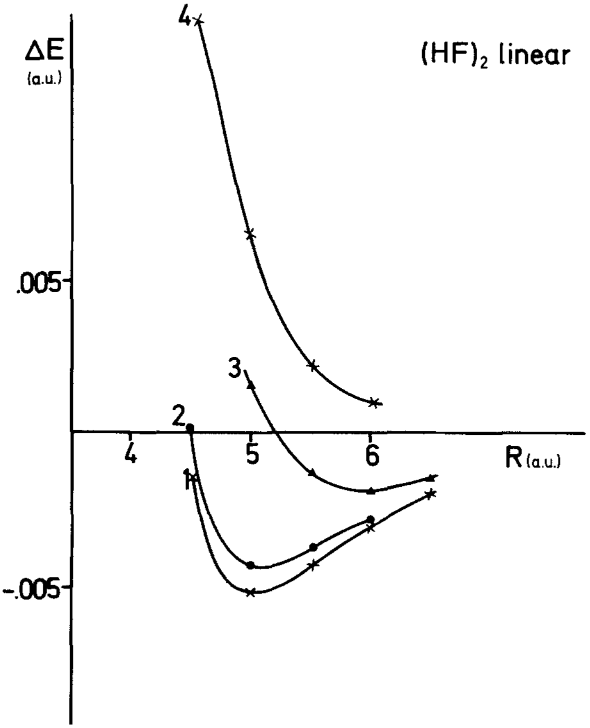


Fig. 1. Curve 1: $\Delta E = E\,\mathrm{dim} - 2\,E_0$. Curve 2: $\Delta E - f\Delta\varepsilon$; $f = 1/6$ for HF, 2/7 for H_2O, 4/11 for HCN. Curve 3: $\Delta E - \Delta\varepsilon \equiv \Delta E$ – basis function correction. Curve 4: $\Delta\varepsilon \equiv$ basis function correction

functions for the dimer; that is, the dimer calculation for a given geometry is repeated first with all the nuclear charges set equal to zero on center 1 and then with all the nuclear charges set equal to zero on center 2. In this way the monomer energies, E_1 and E_2 will contain the "extra" stabilization induced by the increased basis set upon dimerization and the "true" stabilization will be $E_{12} - E_1 - E_2$ rather than $E_{12} - 2E$ (isolated monomer). The difference between $2E$ (isolated monomer) and $E_1 + E_2$ we designate the basis function connection $\equiv \Delta\varepsilon$.

Results and Discussions

In the three cases studied here, a significant lowering of the monomer energy (at reasonable H-bond distances) was obtained in the calculations on the electron donor fragment (1) with the basis functions from the electron acceptor (2). E_2, the monomer energy for the electron acceptor with basis functions from the electron donor, did not differ significantly from the isolated monomer energy.

It is clear from Table 1 that a large portion of the dimerization energy comes from "extra" stabilization. One of the main reasons for this "extra" stabilization is the poor representation of core orbital in a single Slater basis. Thus, the "extra

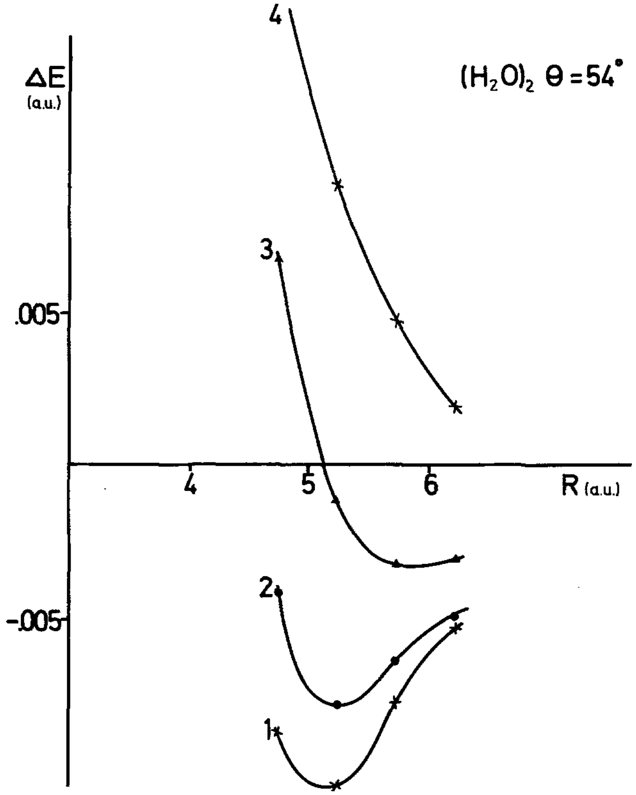


Fig. 2. Curve 1: $\Delta E = E\,\text{dim} - 2\,E_0$. Curve 2: $\Delta E - f\Delta\varepsilon$; $f = 1/6$ for HF, 2/7 for H_2O, 4/11 for HCN. Curve 3: $\Delta E - \Delta\varepsilon \equiv \Delta E$ – basis function correction. Curve 4: $\Delta\varepsilon \equiv$ basis function correction

stabilization" comes mainly from an improvement in the representation of the 1*s* core by the additional basis functions. Support from this comes from the fact that the calculations on the electron acceptor with basis functions of the electron donor show no large stabilization because the orbitals are too far away from the electronegative atom.

However, the fact that for $R = 5.0$ au., the $\Delta\varepsilon$ computed for $(HF)_2$, $\theta = 0°$ is so much less than that for $\theta = 60°$ indicates that the improvement of the 1*s* representation is closely linked to the "charge transfer" of electrons out of the valence shell. Newton and Ehrenson have shown in their study of hydronium ions that an energy optimized representation of the water 1*s* core results in an "extra" stabilization at $R(O–O) = 2.4$ Å of less than 1 kcal/mole, in contrast to the 9.4 kcal/mole "stabilization" found here for water dimer at $R(O–O) = 2.51$ Å, $\theta = 54°$. Thus, it is unlikely that this counterpoise procedure will greatly change the dimerization energy computed with "double zeta" bases and the exaggerated ΔE found in those cases is really due to the overestimated monomer dipole moment.

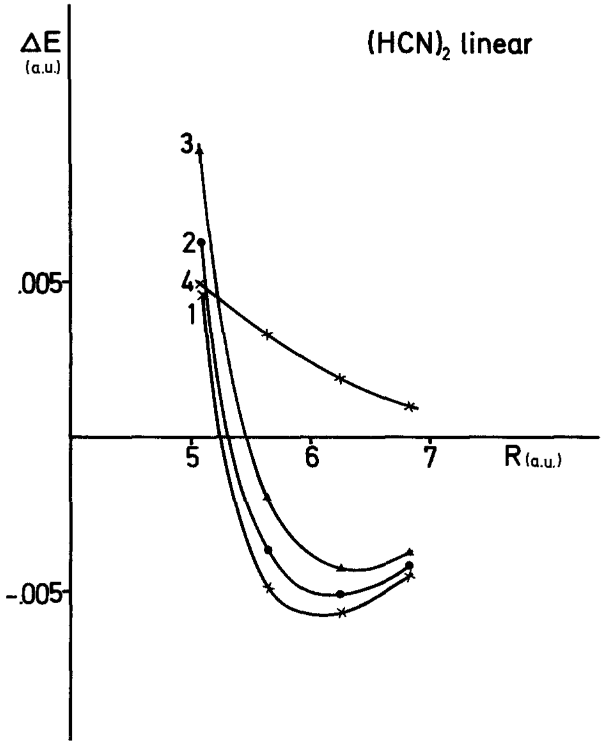


Fig. 3. Curve 1: $\Delta E = E\,\mathrm{dim} - 2\,E_0$. Curve 2: $\Delta E - f\Delta\varepsilon$; $f = 1/6$ for HF, 2/7 for H_2O, 4/11 for HCN Curve 3: $\Delta E - \Delta\varepsilon \equiv \Delta E$ – basis function correction. Curve 4: $\Delta\varepsilon \equiv$ basis function correction

The results of the calculations are presented in Table 1 and graphically summarized in the three figures. It is obvious from Fig. 2 that if the total correction $\Delta\varepsilon$ (defined as the difference between the monomer energies with and without additional basis functions) is added to the uncorrected stabilization energy, the resulting potential curve shows a too small an energy of dimerization and a too large an intermolecular separation as compared with the most accurate calculations; thus, we have somewhat "overcorrected" our original potential curve.

In order to give results in better agreement with the best *ab initio* calculations and experiment an empirical "correction factor" was sought. Since the electron pair acceptor in the actual dimer (in the case of HF) has only one unoccupied orbital and we have included six extra orbitals in the calculation of E_1, each $\Delta\varepsilon$ was multiplied by 1/6 and added to the uncorrected ΔE to give a dimerization energy of 4.4 kcal/mole at $R = 2.6$ Å, $\theta = 60°$. A similar analysis of the water dimer surface (multiplying the $\Delta\varepsilon$ by 2/7) and the HCN surface (multiplication by 4/11) led to the results summarized in Table 2. As one can see, the results, albeit suspect because of our correction factor, are in excellent agreement with the experimental (where available) values and "most accurate" calculations. The "agreement" with experiment is somewhat fortuitous, since no dispersion attraction can be found within the SCF framework.

Table 2. Comparison of counterpoise results with more accurate calculations
Distances in Å and ΔE in kcal/mole

	R(STO-3G)[a]	ΔE(STO-3G)	R(CP)[b]	ΔE(CP)	R(DZ+P)[c]	ΔE(DZ+P)
$(HF)_2\ \theta = 60°$	2.6	5.4	2.6	4.4	2.85[d,e]	4.2[d]
$(H_2O)\ \theta = 54°$	2.7	6.6	2.8	5.0	3.0[f]	4.7[f]
$(HCN)_2$ linear	3.3	3.6	3.3	3.3	3.4	3.3

[a] STO-3G-direct calculation of ΔE. R refers to the minimum energy separation between monomers.

[b] CP – counterpoise $\Delta E - f\Delta\varepsilon$; $f = 1/6$ for HF, 2/7 for H_2O, 4/11 for HCN.

[c] DZ + P – very accurate calculation of molecular potential surface "double zeta + polarization" atomic basis – for $(HCN)_2$ no such accurate calculation exists, so the ΔE is taken from the experimental one in Ref. [6] and the R is assumed to be that of the infinite crystal (Ref. [7]).

[d] See Ref. [8]; the minimum energy geometry occurs at $\theta = 40°$.

[e] See Ref. [9].

[f] See Ref. [10].

Conclusions

The above results indicate that the functional counterpoise method, with a systematically chosen empirical factor, can be useful in improving potential surface calculations carried out with limited *ab initio* bases. No new integrals need be calculated, and with starting vectors from the isolated monomer, the additional SCF calculations converge very rapidly; thus the extra computational effort required to implement the counterpoise method is minimal.

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