ACCURATE EVALUATION OF SCF AND MP2 COMPONENTS OF INTERACTION ENERGIES. COMPLEXES OF HF, OH$_2$, AND NH$_3$ WITH Li$^+$

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Dedicated to Dr R. Zahradnik whose early vision of application of ab initio *methods to the study of molecular interactions had a great impact on developments in biodisciplines and a profound effect upon the research careers of many scientists including the authors.*

High-quality Gaussian basis sets of the well-tempered type, containing three sets of polarization functions on all atoms, are used to investigate the interaction of Li$^+$ with HF, OH$_2$, and NH$_3$. These sets reproduce the SCF and MP2 energies of the various monomers very well and, moreover, accurately treat the multipole moments and polarizabilities of the monomers. When applied to the complexes, the sets are essentially free of primary and secondary basis set superposition error at the SCF level; MP2 extension effects are also completely negligible while basis set superposition effects are small but non-negligible. Analysis of the correlation corrections to the molecular properties, coupled with comparison of the interaction of the bases with a point charge, provides a straightforward explanation of correlation contributions to the interaction energy. Recommendations are provided to guide selection of basis sets for molecular interactions so as to avoid distortion of the various components.

During the period of the late 1970s and early 1980s, there was a burst of optimism concerning accurate calculation of molecular interactions[1-4], occasioned by the rapid advances in computational hardware and software which allowed unprecedented levels of electron correlation to be applied to this problem[5]. More recent work, however, has dampened some of the initial enthusiasm by indications that quantitative accuracy requires basis sets of truly large proportions. As an example, Frisch et al.[6] were unable to reproduce the experimental H-bond energy of the water dimer[7] even when fourth-order perturbation theory was applied to a 6-311++G(3df, 3pd) basis set, containing 162 basis functions in all. Chałasinski and coworkers have demonstrated the need to include polarization functions up to $l = 5$ in order to saturate the dispersion energy of a system as simple as He$_2$[8]. For molecules as simple as H$_2$O or HF, simultaneous saturation of the Hartree–Fock energies and monomer properties requires Gaussian expansions of about 140 basis functions[9]. Hence, recent developments convincingly demonstrate that the basis set problem is far from resolved for molecular interactions.

Let us now consider supermolecular calculations of interaction energies which are forced to resort to a finite basis set. Consistency requires the complex to be represented by the same basis as the individual subunits as originally pointed out by Boys and Bernardi in 1970. However, this is generally not the case since the basis for the complex contains the orbitals of *both* the

individual subunits. Representation of the individual subunits within the full dimer basis set was dubbed the functional counterpoise approach by Boys and Bernardi[10].

Since the addition of the orbitals of a given subunit will lower the energy of its partner, correction of the basis set superposition error by the counterpoise procedure adds an apparent repulsive component to the interaction energy. This correction will typically be rather large for poor basis sets. If the uncorrected interaction energy happens to be fairly close to the experimental result through some fortuitous cancellation of errors, addition of the correction can "worsen" the calculated result[6,11-14]. In fact, a poor basis set would not be expected to produce an accurate interaction energy and the corrected result is entirely appropriate to such a set, even if further removed from experiment.

Nevertheless, the magnitude of the counterpoise correction for poor basis sets, coupled with the fact that the corrected potentials were more repulsive than were hoped for, fueled speculation that the counterpoise procedure overestimates the true variational lowering of the subsystem energy in the basis set of the entire complex[11,13]. A good deal of ingenuity and computational effort has been expended in dispelling this misconception[15,16].

The variational lowering of energy due to the partner's orbitals is magnified at correlated levels. Even in basis sets which are well saturated at the Hartree–Fock level, correlated counterpoise corrections can substantially exceed the true contribution of correlation to the interaction energy[6,14,17]. Indeed, Szalewicz et al.[18] presented results which suggest that the magnitude of the MP2 counterpoise correction can increase as the basis set is enlarged. This finding is not surprising when one considers the difficulty of saturating a two-electron basis set in comparison with its one-electron analog. There have been recent suggestions that (contracted) basis sets optimized against Hartree–Fock atomic energies are inherently poor frameworks for computation of correlation energy. For example, Almlöf and Taylor[19] have proposed using as contraction coefficients the natural orbital expansions from atomic CI calculations as an alternative. (The 6-311G set of Pople and coworkers may serve as another example of a basis set optimized for correlation effects[20].)

Unfortunately, there are no clear recipes for formulation of basis sets which will uniformly treat all the correlation effects in molecular interactions. In light of the slow convergence of dispersion energy, it is advisable to use a number of diffuse polarization functions with high quantum number l. Substantially larger exponents are usually used for proper treatment of intrasystem correlation; however, a larger number of such functions may be required than is customarily employed[19]. Overall, it is clear that more detailed work is warranted since it appears that unsaturation of the intrasystem correlation energy lies at the heart of the large counterpoise corrections noted at correlated levels.

While the counterpoise procedure eliminates the direct consequences of the variational improvements in subsystem energies, it does not remove the influence on the interaction energy terms resulting from modifications in subsystem molecular properties due to the presence of the partner's orbitals. These changes are often termed basis set extension or higher-order basis set superposition effects. Karlström and Sadlej[21] first pointed out that in the supermolecule approach, the properties of each subunit, e.g. moments and polarizabilities, are actually being described within the basis set of the entire complex and not those of the subunits. As one example, consider the interaction between a pair of neutral atoms which obviously contains only a penetration-type Coulomb component. Nevertheless, the presence of the orbitals of atom B leads to a spurious dipole moment on A (and vice versa). Interaction between these two dipoles produces a multipole Coulomb energy (and some changes in the penetration part), purely an artifact of the supermolecule treatment.

The sensitivity of molecular properties to the presence of the partner's orbitals can be surprisingly high. For example, it was found recently[22] that the parallel component of the SCF/

/6-31G** dipole polarizability of NH_3 increases by nearly 3 a.u. (c. 50%) in the presence of the ghost orbitals of a Li^+ cation centered 3 Å from the nitrogen, while the dipole moment rises by 0·17 D, or 10%. With basis set extension effects of this magnitude, the higher-order BSSE may exceed the primary error.

In general, correct description of molecular properties is a necessary condition for a balanced treatment of the polarization terms* in interaction energies. These properties reflect the quality of the wave function in the region distant from the nuclei where the interaction actually occurs. Proper description of this so-called tail region guarantees also an appropriate representation of the exchange terms[15].

The majority of standard basis sets which are optimized against the Hartree–Fock energy are designed to study primarily the geometries of common molecules. Hence, one can hardly expect such basis sets to produce consistent results for interaction energies in weakly bound systems. Yet it was just such an inconsistency that led Schwenke and Truhlar[24] to conclude that counterpoise corrections are of little use. What these authors apparently failed to consider is that a primary difficulty arising from use of various types of basis sets, which the counterpoise procedure cannot correct, is their inconsistent reproduction of monomer properties. Indeed, when the choice of basis set focuses on molecular properties, the corrected interaction energies are vastly more consistent than the uncorrected values for a number of different systems[18,25].

There are thus a number of overriding considerations in selection of a basis set for molecular interactions. It is first necessary to reproduce the various properties of each subunit as accurately as possible so as to correctly describe the nature of the interaction. The sensitivity of these properties to the approach of the partner's orbitals should be minimized in order to diminish the basis set extension effects. Care in these matters should be exercised not only at the SCF but at correlated levels as well. For example, failure to properly describe the correlation corrections to the properties would likely introduce an imbalance into the correlation corrections to the interaction energy. A similar consideration applies to the desired low sensitivity of the computed energy of each subunit to the presence of the orbitals of its partner.

Unfortunately, the various criteria mentioned above are best satisfied by different properties of the basis set. As mentioned above, Hartree–Fock optimized basis sets are no guarantee of proper reproduction of multipole moments and polarizabilities, nor of good correlation energies. On the other hand, a basis set which yields the correct dipole moment may be inappropriate for describing correlation corrections to this moment.

Our goal in the present work is to attempt to take all of the above considerations into account and perform benchmark calculations using basis sets of very high quality, especially designed for molecular interactions. We intend to properly account for all the terms of the interaction energy which occur in the supermolecule approach. The basis sets are chosen also so that the superposition and extension effects will be vanishingly small. Only by minimizing these artifacts can the contents of the supermolecule interaction energies be analyzed with any degree of confidence. The systems selected for study are the interactions between Li^+ and the bases NH_3, OH_2, and HF. The SCF portion of the interaction energy contains all terms present in molecule–molecule systems but is somewhat more amenable to analysis due to the compact, highly nonpolarizable nature of Li^+. This low polarizability effectively precludes

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*   Polarization terms are here defined as those obtained from the polarization RSPT such as Coulomb, induction, dispersion, etc; see Jeziorski and Kołos[23].

any dispersion energy, greatly simplifying the analysis of correlation contributions to the interaction, restricting them mainly to intrasystem type (which are in general less well understood than intersystem terms).

THEORETICAL AND CALCULATIONS

Basis Sets

Huzinaga and Kłobukowski have derived high-quality Gaussian expansions, termed well-tempered, for a number of atoms, including N, O, F, and Li, designed for work within the generalized Raffenetti contraction scheme[26,27]. 15 values of the exponents $(\alpha_1, ..., \alpha_{15})$ were optimized within the 4-parameter well-tempered criterion, maintaining well spaced exponent values common to s, p, d, etc. radial functions. The exponents cover a wide range of values from quite large to very small. The latter are diffuse enough so that no additional "soft" functions are necessary. A basis set of this type is expected to be much better than often-used smaller sets which are augmented by diffuse functions chosen in a more or less random fashion.

Only exponents $1 - 14$ are used in the s-set; α_6 through α_{15} are used within the p-set. The $(14s, 8p)$ set was contracted for N, O, and F to $[7s, 6p]$ according to the contraction scheme optimized by Kłobukowski et al.[28] and displayed in Table I. Note that the last 5 s-orbitals share exponents with the first 5 p-functions. Also, the exponents are repeated in different contractions, providing the advantage of generalized contraction within the framework of segmented contraction available in most computer codes. The scheme used for Li was slightly different than for the other three atoms, and reproduced the Hartree–Fock limit of Li^+ with accuracy much better than $0 \cdot 1$ μH (1 H = 2 625·5 kJ/mol). Huzinaga's 10s expansion of H (ref.[29]) was contracted as reported in Table I.

TABLE I
Orbital contraction scheme

Orbital	N, O, F	Li	H	Orbital	N, O, F	Li
1s	$\alpha_1 - \alpha_5$	$\alpha_1 - \alpha_6$	$\alpha_1 - \alpha_5$	1p	$\alpha_6 - \alpha_{10}$	α_{10}
2s	$\alpha_6 - \alpha_{12}$	$\alpha_7 - \alpha_8$	$\alpha_6 - \alpha_7$	2p	α_{11}	α_{11}
3s	$\alpha_6 - \alpha_{10}$	$\alpha_9 - \alpha_{10}$	α_8	3p	α_{12}	α_{12}
4s	α_{11}	α_{11}	α_9	4p	α_{13}	α_{13}
5s	α_{12}	α_{12}	α_{10}	5p	α_{14}	α_{14}
6s	α_{13}	α_{13}		6p	α_{15}	
7s	α_{14}	α_{14}				

One of the most attrative features of the well tempered basis sets is the capability of sharing of exponents between s, p, d, f types of functions. For example, using the four or five lowest exponents for the d-functions would provide a wide range of values; the compact functions would provide an adequate framework for intra-atomic correlation while the smaller exponents would permit a good description of polarizability, dispersion, etc. However, since computational resources restrict us to 3 sets of d-functions, we followed the suggestion of Werner and Meyer in choosing their exponents[30]. α_E, the exponent of the first d-function, was derived by maximizing $E^{(2)}$, the second-order Møller–Plesset perturbation correlation energy of each subunit; the values obtained are reported in Table II. Maximization of the transverse component of the dipole polarizability of NH_3, OH_2, and HF (perpendicular to the principal symmetry axis; this component saturates most slowly) led to a second exponent, herein denoted as α_{pol}. Werner and Meyer predict the ratio α_E/α_{pol} will typically be ~ 8, quite close to our own findings here. In addition to α_E which was used unmodified, the exponents chosen for the other two d-functions were $(2/3)\,\alpha_{pol}$ and $2\alpha_{pol}$, leading to a set of three well-spaced d-exponents. The latter value assures a good representation of the dipole moment[30]. A similar procedure was used to obtain the exponents of the three p-functions of hydrogen, optimized for HF and then applied to all three systems. All the exponents of polarization functions are listed in Table II.

Due to the compact nature of its charge distribution, the Li^+ ion is quite unpolarizable and its basis set was hence augmented only by polarization functions of p-type.* Although the absence of d-orbitals limits the amount of angular correlation that can be recovered, this feature is not particularly important from the perspective of molecular interactions which we are studying here. We should note that even without d-functions, the correlation energy calculated for Li^+ with our $[7s5p]$ basis set (see Table III) is about 70 times larger than that obtained with the standard 6-31G* basis which does include a d-function. The frozen-core approximation was used in calculating the properties described below whereas no orbitals were frozen when computing the interaction energies. Pure spherical harmonic d-functions were used throughout. With respect to geometries, experimental bond distances and angles were used which are identical to those adopted in previous property calculations[30,32] so as to facilitate comparisons (for HF $r = 1.7325a_0$; for H_2O $r_{OH} = 1.808847a_0$, $\Theta(HOH) = 104.524°$; for NH_3 $r_{NH} = 1.9132a_0$, $\Theta(HNH) = 107.66°$).

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* The very low polarizability of Li^+ may be appreciated by the following comparison. Although this set containing p-functions allows only for dipole polarizability, this quantity is exceedingly low for Li^+ at the SCF level (our finite field value is 0.1885 au, compared to the best CHF result of 0.1896 (ref.[31])), more than 7 times smaller than the SCF dipole polarizability of isoelectronic He.

Molecular Properties

Quite frequently, basis sets which accurately reproduce the molecular properties do so at the expense of the total energy at the SCF level[30,32], a factor which generally leads to large basis set superposition error in the complex (and also to inaccurate monomer geometries). As illustrated by the results presented in Tables III — V, such is not the case with our basis sets. For example, the SCF energies reported in the first column of Table III are within several mH of the Hartree–Fock limit, listed in the succeeding column. Our wavefunction for water yields the same SCF energy as a 39-term STO function; the corresponding $E^{(2)}$ represents 97% of the total obtained with this function[33]. We expect results of similar quality for the remaining hydrides. The next several columns illustrate that despite the cutoff of the perturbation expansion at second-order, our MP2 energies are within about 75% of the estimated total correlation energies.

The values calculated at the SCF and MP2 levels for the dipole moment and polarizability tensor elements are reported in Table IV along with previous calculated and experimental data for purposes of comparison. Our SCF values compare quite favorably with the previous calculations of Werner and Meyer (WM) who used

TABLE II

Exponents of polarization d-functions (heavy atoms); p-functions on H are 1·0, 0·316, 0·1

Molecule	α_E	$2\alpha_{pol}$	$(2/3)\,\alpha_{pol}$
HF	1·74	0·46	0·153
OH_2	1·25	0·30	0·10
NH_3	0·9	0·22	0·075

TABLE III

Total SCF and correlation energies (a.u., 1 a.u. $=$ 2 625·5 kJ/mol) of subunits

Molecule	E^{SCF}	$E(\lim)^a$	$E^{SCF} - E(\lim)$	$E^{(2)}$	$E^{corr}(\lim)^b$	% corr
HF	−100·06834	−100·0706	0·0023	−0·28423	−0·379	75
OH_2	−76·06423	−76·0675	0·0033	−0·27309	−0·372	73
NH_3	−56·22185	−56·226	0·004	−0·24762	−0·334 ± ·004	74
Li^+	−7·23641	−7·23641	0·0000	−0·02764		

[a] Hartree–Fock limit quoted after ref.[9] for all except Li^+; *[b]* quoted after ref.[9]

TABLE IV
Computed dipole moment and polarizability tensor[a] elements (a.u.)

Method	HF			OH$_2$			NH$_3$		
	this work	DRS[b]	WM[c]	this work	DRS[b]	WM[c]	this work	DS[d]	WM[c]
				μ					
SCF	0·7569	0·7568	0·757	0·7800	0·7801	0·782	0·6368	0·6370	0·635
(2)	−0·0492	−0·0490		−0·0514	−0·0518		−0·0394	−0·0375	
SCF + (2)	0·7077	0·7078		0·7286	0·7283		0·5974	0·5995	
expt[e]	0·707			0·724			0·594		
				α_{xx}					
SCF	4·466	4·48	4·47	7·898	7·91	7·99	12·776	12·76	13·03
(2)	0·807	0·85		1·661	1·73		0·943	0·98	
expt[e]	5·08			9·19 ± 0·09			13·86, 13·96[f]		
				α_{yy}					
SCF	4·466	4·30	4·47	9·163	9·17	9·04	12·776	12·76	13·03
(2)	0·807	0·85		0·835	0·85		0·943	0·98	
expt[e]	5·08			9·68 ± 0·09			13·86, 13·96[f]		
				α_{zz}					
SCF	5·739	5·74	5·75	8·478	8·51	8·47	13·323	13·12	13·98
(2)	0·650	0·66		1·211	1·26		2·361	2·42	
expt[e]	6·40			9·47 ± 0·09			15·95, 15·74[f]		

[a] z-Direction coincides with principal symmetry axis; x and y coordinates are equivalent for NH$_3$ and HF and represent perpendicular directions. x-axis is perpendicular to molecular plane of H$_2$O; [b] from Diercksen, Roos, and Sadlej[34]; [c] from Werner and Meyer[30]; [d] from Diercksen and Sadlej[35]; [e] vibrationless estimate quoted after refs[34,35] with vibrational corrections estimated in ref.[30]; [f] both values are vibrationless estimates quoted after ref.[32], with vibrational corrections estimated in ref.[30].

a $[11s6p3d]$ basis set, reportedly essentially uncontracted in the valence region for heavy atoms. Moreover, they are in very good agreement with the state-of-the-art results of Sadlej et al.[34,35], calculated with a $(12s8p3d1f)$ basis set contracted to $[8s5p3d1f]$. The only appreciable discrepancy resides in the polarizability of NH_3 which is somewhat smaller than Werner and Meyer's results (neither were Diercksen and Sadlej able to reproduce the latter data).

The correlation contributions to the molecular properties are generally in very good agreement with previous results, another indication of the quality of the reference function. These contributions are very important as they play a dominant role in determining the values of the MP2 correction to the interaction energy (see below) and hence should be carefully examined.

As seen from the footnotes in Table V, the quadrupole moments differ from the best Hartree–Fock values by about 0·1 a.u. This discrepancy is perhaps disappointing since it indicates good reproduction of this property requires f-type polarization functions, as demonstrated by previous work[9,36].

The susceptibility of the molecular properties to basis set extension effects may be checked by evaluating the multipole moments within the dimer basis set. The values computed at the SCF level for the dipole and quadrupole moment of the bases in the presence of the ghost orbitals of Li^+ at a distance R from the base, along its principal symmetry axis, are listed in Table V. Approach of these ghost orbitals from infinity to as close as 2 Å from the heavy atom has a negligible effect $(0·01 - 0·05\%)$ on the dipole moments. The quadrupole moments change to only a slightly greater degree, remaining within $0·05\% - 0·5\%$ of their values in the absence of the ghost

TABLE V

SCF dipole and quadrupole moments^a (a.u.) calculated including ghost orbitals of partner Li^+

R Å	HF		OH_2			NH_3	
	μ	Q_{zz}	μ	Q_{xx}	Q_{yy}	μ	Q_{zz}
2	0·7570	1·8809	0·7810	1·8156	−1·9228	0·6371	−2·0000
3	0·7569	1·8807	0·7811	1·8152	−1·9263	0·6370	−2·0030
4	0·7569	1·8803	0·7811	1·8151	−1·9265	0·6369	−2·0072
5	0·7569	1·8802	0·7810	1·8151	−1·9265	0·6368	−2·0091
∞	0·7569	1·8800^b	0·7810	1·8151^c	−1·9265^c	0·6368	−2·0101^d

^{a} With respect to heavy atom; ^{b} center of mass value is 1·6182; numerical H–F value is 1·7321; exp: 1·7; ^{c} center of mass values: $Q_{xx} = 1·9880$, $Q_{yy} = -1·7536$; estimated H–F limit: $Q_{xx} = 1·899$; exp: $Q_{xx} = 1·96 \pm 0·01$; ^{d} center of mass value: $-2·2856$; estimated H–F limit: $-2·159$; exp: $-2·42 \pm 0·04$.

orbitals. (The corresponding spurious dipole moment of Li^+ is exceedingly small, only c. 10^{-7} a.u., and may hence be neglected.) The C_2 and C_3 Coulomb coefficients will change by the same proportional amount when the full basis set is employed, leading to a combined error in the Coulomb energy of less than 0.2% through R^{-3}. We therefore conclude that our electrostatic interaction energies are essentially uncontaminated by basis set extension effects. Note also that due to the greater sensitivity of the quadrupole moment to basis set extension, the charge-dipole term cannot be used by itself[22] to provide an accurate measure of the basis set extension effects in the Coulomb term since it yields only 10% of the full effect, nor should it serve as an estimate of the total secondary BSSE[22].

Perhaps a more complete and accurate estimate of the effects of the partner orbitals upon the Coulomb energy can be arrived at by computation of the electrostatic potential produced by the base molecule in the position where the Li^+ occurs. Since Li^+ is an isotropic cation, this potential is equivalent to the total Coulomb energy of interaction (neglecting penetration). The columns headed by the title "B" in Table VI contain the value calculated when only the orbitals of the base B are present; comparison with the data in the next column labeled $B \cdot \cdot Li^+$ illustrates the influence of the Li^+ orbitals. If we neglect the penetration, the first column corresponds to the correct Coulomb energy of $B \cdot \cdot Li^+$ while the second represents the Coulomb energy of the same system, affected by basis set extension. Discrepancies between the two columns do not exceed 0.2%, the value estimated above from the multipole expansion through the charge-quadrupole term. This analysis provides further verification of the small magnitude of higher-order BSSE with our basis set.

As a final check, we also computed the magnitude of the basis set extension effect upon the SCF polarizability as well as correlation corrections to the polarizabilities

TABLE VI
Coulomb energy (kcal/mol)^a of $B \cdot \cdot Li^+$, $\varepsilon_{Coul}^{(10)}$. R represents the distance between Li^+ and the heavy atom along the principal symmetry axis. "B" and "$B \cdot \cdot Li^+$" indicate the basis set in which the Coulomb energy was calculated

R $Å^b$	HF		OH_2		NH_3	
	B	$B \cdot \cdot Li^+$	B	$B \cdot \cdot Li^+$	B	$B \cdot \cdot Li^+$
2	-17.41	-17.40	-29.34	-29.43	-40.27	-40.17
3	-9.675	-9.672	-14.12	-14.11	-17.52	-17.48
4	-6.047	-6.044	-8.153	-8.153	-9.275	-9.324
5	-4.120	-4.120	-5.292	-5.292	-5.728	-5.727

^{a} 1 kcal/mol $= 4.184$ kJ/mol; ^{b} 1 Å $= 10^{-10}$ m.

and the dipole moments. As second-order properties, they should be more highly sensitive to the presence of the ghost orbitals. When the Li^+ ghost orbitals were placed 2 Å from HF, a distance where these effects would be expected to be quite large, the SCF polarizability and the MP2 contribution to the dipole moment were not affected at all; the correlation corrections to the components of the polarizability tensor were altered by a fraction of 1%.

As noted earlier, we used a set of polarization function exponents optimized against correlation energy and polarizability. It was deemed of interest to examine what sort of results would be obtained if we had instead used the exponents of the well-tempered sets. We therefore checked two different sets of 3 d-exponents for HF: The lowest three (0·2348, 0·5728, 1·3780) and the next lowest (0·5728, 1·3780, 3·309). (The latter set of three has been recommended by Kłobukowski et al. for energy calculations.) The first set is fairly similar to our optimized exponents, only slightly more compact in the lower exponents. It is hence not surprising that the computed α_{xx} of 4·351 is rather close to the value reported in Table IV; $\mu^{(2)}$ is also nearly identical. Despite a somewhat greater valence correlation energy (by 0·02 a.u.), the more compact second set causes a deterioration of α_{xx}, yielding a value of only 3·649 while $\mu^{(2)} = = -0·0471$. We might conclude that the first triplet would suffice and has the added advantage for computational efficiency of shared exponents with the s, p set.

Let us finally note that low polarization exponents do not automatically guarantee proper description of polarizability. For example, in another calculation of HF we used a sequence of d-function exponents 8α, 2α, $2\alpha/3$ where $\alpha = 0·09$, a slightly larger value than the smallest p-exponent 0·077 of F. The transverse component of the polarizability was found to be slightly smaller (4·44 a.u.) than with our optimized set (4·47 a.u.).

Interaction Energies

In considering the interaction of a base with Li^+, it is instructive to compare with the result calculated when the Li^+ is replaced with a positive point charge, i.e., a proton, p^+, having neither orbitals nor electrons. The SCF interaction energy of $B\cdot\cdot Li^+$ is comprised of Coulomb and induction terms plus their exchange counterparts. The exchange effects are absent in $B\cdot\cdot p^+$, as are the penetration parts of Coulomb and induction energies. Since the penetration terms should be negligible due to the highly compact nature of Li^+, and since the basis set extension effects upon the Coulomb energy have been demonstrated above to be extremely small, it is safe to assume that the Coulomb energies of interaction of a base with Li^+ and p^+ are essentially identical. In the case of the induction energy, contributions of the sort $B \rightarrow Li^+$, designating polarization of Li^+ by the base, can be safely ignored due to the very small polarizability of Li^+. The remaining component. representing the inductive effect of the cation on B, will be similar for either Li^+ or p^+.

At the MP2 level, the supermolecular interaction energies are as follows[37]:

$$B\cdot\cdot Li^+: \Delta E_{MP}^{(2)} = \varepsilon_{Coul}^{(12)} + \varepsilon_{exch}^{(12)} + \varepsilon_{disp}^{(20)} + \varepsilon_{exch-disp}^{(20)} +$$

$$+ \text{ induction correlation } (Li^+ \rightarrow B) \qquad (1)$$

$$B\cdot\cdot p^+: \Delta E_{MP}^{(2)} = \varepsilon_{Coul}^{(12)} + \text{ induction correlation } (p^+ \rightarrow B), \qquad (2)$$

where the subscripts and superscripts have their usual meaning. "Induction correlation" denotes changes in the induction energy due to intrasystem correlation. The uncoupled Hartree–Fock (UCHF) dispersion term $\varepsilon_{disp}^{(20)}$, along with its exchange counterpart, should be quite small in Eq. (1), again due to the very low polarizability of Li^+ (0·1885 a.u.). Taking into account the above assumptions, the differences between the correlation corrections to the Li^+ and p^+ interaction energies, Eqs (1) and (2), can be attributed mainly to exchange effects.

The calculated interaction energies of the three bases with Li^+ are reported in Table VII, both with and without counterpoise correction. While extremely small at the SCF level (less than 0·01 kcal/mol), the MP2 counterpoise corrections are considerably larger, 0·07, 0·16, and 0·28 kcal/mol for HF, H_2O, and NH_3 at $R = 2$ Å, respectively. Nevertheless, the BSSE remains even in this case a rather small fraction of the total MP2 contribution to the interaction energy.

The strength of the interaction follows the order $NH_3 > OH_2 > HF$, consistent with the trend in basicity. Electron correlation is generally destabilizing, with one exception to be discussed below.

The columns labeled p^+ pertain to the interaction energy calculated when Li^+ is replaced by a proton. Comparison with the data in the preceding columns demonstrates near coincidence for distances of 3 Å or more, particularly with the counterpoise-corrected Li^+ interaction energies. The distance at which the Li^+ and proton data begin to diverge is somewhat larger for NH_3, c. $3-4$ Å. Closer approach leads to a more attractive potential for the proton since the repulsive exchange forces are absent in this case.

It is interesting that the MP2 contribution to the interaction energy of NH_3 with either Li^+ or a proton becomes negative and passes through a minimum at approximately $R = 3$ Å. In the case of H_2O, correlation makes a destabilizing contribution to its interaction; the behavior with a proton shows a maximum at about 3 Å.

Further analysis of the correlation contribution to the interaction in the proton case helps explain these curious trends. The leading $C_2^{(2)}$ term in the multipole expansion of $\varepsilon_{Coul}^{(12)}$ is proportional to the correlation correction to the dipole moment of the base. As noted earlier in Table IV, $\mu^{(2)}$ is negative, and thus $C_2^{(2)} = -\mu^{(2)}$ adds a repulsive component to $\varepsilon_{Coul}^{(12)}$.* This term is dominant at long distances and ex-

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* From the values of the second-order correlation corrections to the quadrupole moments of refs[34,35], it is anticipated that the Coulomb $C_3^{(2)}$ coefficients will also be repulsive for HF, H_2O, and NH_3.

plains the positive contributions to $\Delta E_{MP}^{(2)}$ at $R = 4$ or 5 Å for all bases. At the same time, however, second-order correlation effects increase the polarizability of each base (see Table IV), thus enhancing the attractive induction component through $C_4^{(2)} \approx -\bar{\alpha}^{(2)}$. Due to the R^{-4} dependence of the latter term, it becomes progressively more important at short range and eventually causes $\Delta E_{MP}^{(2)}(p^+)$ to decrease as the proton approaches OH_2. The particularly large value of $\alpha^{(2)}$ for NH_3 permits the correlation-enhanced induction energy to overwhelm the repulsive contribution from $\varepsilon_{Coul}^{(12)}$, leading to the negative values of $\Delta E_{MP}^{(2)}(p^+)$ for this base in Table VII. The effects are quite similar when Li^+ replaces the proton, except for the repulsive exchange energy which becomes important in the $2-3$ Å range. The combination of a large negative value of $\mu^{(2)}$ for HF and a fairly small $\bar{\alpha}^{(2)}$ lead to the repulsive character of $\Delta E_{MP}^{(2)}$, particularly for the proton at $R = 2$ Å.

One can estimate the induction energy for $B \cdots p^+$ by subtracting the electrostatic energy in Table VI from the total $\Delta E^{SCF}(p^+)$ in Table VII. At any distance R, the induction energies for the three bases $NH_3 : OH_2 : HF$ are in the approximate ratio $4 : 2 : 1$, obeying the same trends as the polarizabilities of the bases.

TABLE VII

Interaction energies^a (kcal/mol) computed for $B \cdots Li^+$ and $B \cdots p^+$

R Å	ΔE^{SCF}		$\Delta E_{MP}^{(2)}$	
	Li^+	p^+	Li^+	p^+
		$B = HF$		
2	$-21\cdot98\ (-22\cdot00)$	$-25\cdot45$	$1\cdot50\ (1\cdot43)$	$1\cdot27$
3	$-11\cdot16\ (-11\cdot17)$	$-11\cdot18$	$0\cdot743\ (0\cdot724)$	$0\cdot760$
4	$-6\cdot523\ (-6\cdot526)$	$-6\cdot523$	$0\cdot464\ (0\cdot456)$	$0\cdot468$
5	$-4\cdot318\ (-4\cdot320)$	$-4\cdot318$	$0\cdot311\ (0\cdot307)$	$0\cdot311$
		$B = OH_2$		
2	$-33\cdot82\ (-33\cdot83)$	$-44\cdot40$	$1\cdot68\ (1\cdot52)$	$0\cdot350$
3	$-16\cdot60\ (-16\cdot61)$	$-16\cdot83$	$0\cdot578\ (0\cdot546)$	$0\cdot547$
4	$-8\cdot952\ (-8\cdot953)$	$-8\cdot948$	$0\cdot410\ (0\cdot395)$	$0\cdot430$
5	$-5\cdot613\ (-5\cdot613)$	$-5\cdot612$	$0\cdot296\ (0\cdot291)$	$0\cdot298$
		$B = NH_3$		
2	$-40\cdot18\ (-40\cdot19)$	$-66\cdot46$	$1\cdot51\ (1\cdot23)$	$-0\cdot391$
3	$-21\cdot84\ (-21\cdot85)$	$-23\cdot18$	$-0\cdot060\ (-0\cdot112)$	$-0\cdot546$
4	$-10\cdot84\ (-10\cdot85)$	$-10\cdot85$	$0\cdot018\ (-0\cdot004)$	$0\cdot032$
5	$-6\cdot303\ (-6\cdot304)$	$-6\cdot297$	$0\cdot101\ (0\cdot090)$	$0\cdot110$

^{a} Values in parentheses are uncorrected by counterpoise procedure; 1 kcal/mol $= 4\cdot184$ kJ/mol.

As mentioned earlier, the difference between ΔE for the proton and Li^+ is largely due to exchange effects in the latter. For $R = 2$ Å, this difference at the SCF level ranges from a minimum of 3·5 kcal/mol for HF to a maximum of 26·3 kcal/mol for NH_3. The MP2 differences are somewhat smaller, lying between 0·2 (HF) and 1·9 (NH_3) kcal/mol. (Since the Li^+ MP2 interaction contains a small amount of attractive dispersion energy, the latter values represent lower bounds to the true exchange effects.) It is important to stress that at this short distance, the cumulative correlation exchange effects greatly exceed their polarization counterparts for H_2O and NH_3.* From the formal point of view, correlation corrections to the exchange terms are considerably more difficult to evaluate directly than are polarization terms. It is hence of prime importance to determine the magnitude of the error incurred by neglecting these effects. Since there are no exchange terms present when Li^+ is replaced by a proton, addition of $\Delta E_{MP}^{(2)}(p^+)$ to $\Delta E^{SCF}(Li^+)$ provides a good estimate of the total interaction energy of a base with Li^+ in the absence of correlation corrections to the exchange terms. The rather small differences between the last two columns of Table VII, coupled to the much more dramatic variation of ΔE^{SCF} with R, lead us to conclude that the above exchange corrections are not essential to good accuracy. The reader is cautioned, however, against generalizing this finding to interactions between neutral molecules which are characterized by much stronger overlap and substantially shallower ΔE^{SCF}. Neglect of $\varepsilon_{exch}^{(12)}$ would likely have a significant effect upon the position of the minimum in such complexes.

CONCLUSIONS

As a result of our careful selection of basis set, we believe we have produced a set of interaction energies that are virtually undistorted by primary and secondary superposition error. Moreover, the accurate reproduction of the molecular properties suggests that the individual components of the interaction energies are faithfully represented. For future applications in molecule–molecule interactions such as H-bonds, we would recommend adding a single set of f-functions with a small exponent which maximizes the quadrupole polarizability (e.g. by the procedure described in literature[36]); a second set to fine-tune the quadrupole moments would further improve the results. Satisfactory treatment of the quadrupole polarizability would be particularly useful in attempts to reproduce the C_8 and C_{10} portions of the dispersion energy. Successful reproduction of a given multipole polarizability usually insures proper representation of the correlation correction to the respective multipole moment, since both belong to the same class of second-order properties. Previous attempts to obtain the exponents of the polarization functions have focused on

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*   From the values of the second-order correlation corrections to the quadrupole moments of refs[34,35], it is anticipated that the Coulomb $C_3^{(2)}$ coefficients will also be repulsive for HF, H_2O, and NH_3.

minimization of the dispersion energy $\varepsilon_{disp}^{(20)}$ through the Hylleraas variational principle[38]. While this is very effective for spherically symmetric atoms, the net result of such a procedure for interacting molecules is likely to be optimization of secondary BSSE instead.

Our fairly long "isotropic" sp-sets provide insurance that there are essentially on improvements of the monomer energies due to the partner's diffuse polarization functions. However, this approach is not a sufficient safeguard for the correlated level where the BSSE was found here to rise as we progress from HF to NH_3. However, if one considers that in $H_3N\cdot\cdot Li^+$ the cation is already "buried" in the lone pair of N, i.e. it resides at a "chemical distance", the latter error may be viewed as quite small. Moreover, judicious choice of well-spaced $3d$ and $3p$ polarization functions effectively precludes additional improvement of dipole polarizability by the orbitals of the partner. The latter orbitals may contribute strongly to quadrupole polarizability which is insufficiently described due to the lack of f-functions. However, the energetic consequences of this contamination should be fairly minor except at very short distances.

In some previous calculations of interaction energies a large set of polarization and diffuse sp-functions was added to an isotropic set such as 6-311G which does not describe the core very well, resulting in poor monomer energies (and geometries). Although such an approach would most likely lead to a very good description of molecular properties, the energies of each subsystem will substantially decrease when the partner functions are added. On the opposite end are basis sets for molecular interactions which are prepared by minimization of monomer energies which are optimized in a molecular setting[39,40], a prescription which tends to lower the primary BSSE. Since a small value of BSSE is no guarantee of a balanced description of the interaction energy, modification of the isotropic part of the basis set so as to diminish its sensitivity to ghost orbitals can lead to an overly rigid set which cannot treat second-order properties correctly. In such a case, large basis set extension effects may occur, distorting the polarization terms at the SCF and correlated levels.

The foregoing analysis has shown that the smallness of the correlation contribution to ΔE is due to cancellation among terms of different sign. The correlation correction to the exchange terms and $\varepsilon_{Coul}^{(12)}$ are both positive while the correlation correction to the induction energy is attractive. An improper balance amongst these terms could produce an incorrect sign for $\Delta E_{MP}^{(2)}$, as seen in prior calculations (refs[1,22,41,42], see also discussion in ref.[43]).

The rather large magnitude of the induction effects in $\Delta E_{MP}^{(2)}$ is somewhat disappointing since these effects cannot be rigorously interpreted within the framework of intermolecular perturbation theory[23], adding complexity to analysis of supermolecular results[37]. However, this problem should be alleviated to a large extent when considering interactions between neutral molecules where the induction deformation is much smaller than in the cation–molecule case discussed here.

Our crude estimates of the correlation corrections to exchange terms lead us to believe that these effects are quite small in cation–molecule interactions, not surprising in light of the small overlap. In fact, total neglect of these effects would lead to no qualitative changes. We hesitate to extend this conclusion to molecule–molecule interactions such as H-bonds and charge-transfer complexes with their stronger overlap, however. Although the $\varepsilon_{exch}^{(12)}$ correction has not yet been computed directly except for atoms, there are reasons to expect it will be comparable in magnitude to $\varepsilon_{Coul}^{(12)}$ (see also discussion in literature[18]), perhaps even larger in the vicinity of the vdW minimum and increasing rapidly for closer approach. Hence, incorrect intersubunit separations may result if this term is not properly included.

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