ADIABATIC POLARIZATION POTENTIALS FOR THE WATER AND NITROGEN

MOLECULES. A COMPARISON OF LARGE AND SMALL BASIS SETS.

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I.   INTRODUCTION

     Electrostatic potentials play an important role in a wide range of chemical applications ranging from biochemistry, where they are used in modeling large-molecule interactions and reactivity, to molecular physics, where model potentials are employed in quantum mechanical studies of electron scattering. In both of these applications, the electrostatic potential is only an approximation to the true interaction potential. A better approximation to the interaction potential is obtained by allowing for charge polarization of the target molecule by the reactive partner or scattering particle. In this chapter we focus on this charge-polarization aspect, and, in particular, we study how adiabatic charge polarization affects the interaction potentials for electron-molecule scattering. The general topic of electron-molecule interaction potentials is discussed in detail in the previous chapter in this book. In brief

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review, the effective potential for describing an electron–molecule collision is written as

$$V^{SEP} = V^S + V^E + V^P \tag{1}$$

where V^S is the static potential describing the coulombic interaction of the scattering electron with the unperturbed charge density of the target molecule, V^E is the exchange potential which can be modeled in various ways, and V^P is the polarization potential describing the difference of the interaction of the scattering electron with the relaxed charge distribution and with the unperturbed one. The term V^S is simply the negative of the electrostatic potential discussed in other chapters of this book; in the context of electron–molecule interactions it is called the static potential. The term V^E will not be considered further in this chapter. The term V^P can be written as

$$V^P = V^{Pa} + V^{Pna} \tag{2}$$

where V^{Pa} is the adiabatic polarization potential and V^{Pna} is the correction term for nonadiabatic effects. The term V^{Pna} depends on the scattering energy and is quite difficult to determine; as yet, it has not been calculated accurately. In this paper we discuss calculations of V^S and V^{Pa} from *ab initio* wave functions for three systems: H_2O, N_2 and Ne. We describe our computational methods for determining V^S and V^{Pa} and we present results using very large basis sets for H_2O and Ne. Large basis set results for N_2 have been presented elsewhere already.[1] These results provide information on the importance of including polarization effects in describing the interaction of a charge with a molecule. Since there is great interest in the question of how accurately electrostatic potentials can be calculated using minimum basis sets, we also calculated the static and adiabatic polarization potentials using a minimum basis set for all three systems. In particular, we used the popular STO-3G basis.[2] Comparison with the results using the large basis sets clearly delineates both the deficiencies and the successes of the smaller, more popular basis.

Interactions of electrons with water are very important in the radiation chemistry of aqueous solutions (the major important process is electron–impact ionization),[3-5] and interactions of other charged species with water are very important in inorganic, organic, and biological chemistry. The atom Ne is-of interest because it is isoelectronic with water, while N_2 is a good test case because it is a simple non–hydride. Water and nitrogen are small enough molecules so that large basis sets can be employed to provide accurate results; these accurate results in turn can be

used to test the adequacy of smaller basis sets for determining the
potential terms of interest. We have previously used large basis
sets to calculate static and adiabatic polarization potentials for
H_2[6] and Li_2[7] as well as N_2.[1]

Although our calculations refer directly to electron-molecule
interactions and scattering, they are also relevant to the problem
of interaction potentials of molecules with charged species in
general.

II. THEORY

We define our Cartesian coordinate system with the origin at
the center of mass and the z axis along the appropriate symmetry
axis (the C_2 axis for H_2O and the C_∞ axis for N_2). We then write
our fixed-nuclei Hamiltonian as[6]

$$H_o = H_o^{el} + H_N \tag{3}$$

where H_o^{el} is the electronic Hamiltonian

$$H_o^{el} = \sum_i \left(\frac{-\nabla_i^2}{2} - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \right) + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \tag{4}$$

and H_N is the nuclear repulsion term.

$$H_N = \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \tag{5}$$

In the equations, r_{ij}, $r_{i\alpha}$ and $R_{\alpha\beta}$ denote the distances between
electrons i and j, electron i and nucleus α, and nuclei α and β,
respectively. We first perform a matrix Hartree-Fock (HF) self-
consistent-field (SCF) molecular orbital calculation[8] for a given
molecular geometry. This yields a molecular wave function Ψ_o and
the corresponding energy

$$E_o = \langle \Psi_o | H_o | \Psi_o \rangle \tag{6}$$

Next we add a negative unit test charge at r which gives a pertur-
bation Hamiltonian

$$H_1(r) = \sum_i \frac{1}{|\vec{r}_\alpha - \vec{r}|} - \sum_\alpha \frac{Z_\alpha}{|\vec{r}_\alpha - \vec{r}|} \tag{7}$$

The first term in equation (7) corresponds to the repulsive inter-
action of the test charge with the molecular electrons, and the
second term describes the attractive interaction with the nuclei.
(Note that the terms have the opposite sign as compared to the
corresponding term describing the interaction of a positive test
charge as described in most of the other chapters in this book.)
The first-order interaction energy is

$$E_1(\vec{r}) = <\Psi_o|H_o + H_1(\vec{r})|\Psi_o> \tag{8}$$

where the energy is being evaluated for the unrelaxed charge distri-
bution. This energy is obtained at the beginning of the first
iteration of a new SCF calculation including the term in equation
(7) in the Hamiltonian if the unperturbed wave function Ψ_o is used
as the starting point for the new calculation. Additional itera-
tions to convergence correspond to re-optimizing the electronic
wave function in the presence of the test charge. This gives the
adiabatically perturbed wave function $\Psi_1(\vec{r})$, relaxed orbital
energies $\varepsilon_k(\vec{r})$, and a final energy for the system:

$$E_2(\vec{r}) = <\Psi_1(\vec{r})|H_o + H_1(\vec{r})|\Psi_1(\vec{r})> \tag{9}$$

Note that all of these quantities depend on the position $\vec{r}$ of the
perturbing test change.

      In terms of the above energies we obtain the static potential
as

$$V^S(\vec{r}) = E_1(\vec{r}) - E_o \tag{10}$$

the adiabatically polarized potential as

$$V^{SPa}(\vec{r}) = E_2(\vec{r}) - E_o \tag{11}$$

and the adiabatic polarization potential as

$$V^{Pa}(\vec{r}) = E_2(\vec{r}) - E_1(\vec{r}) \tag{12a}$$

$$= V^{SPa}(\vec{r}) - V^S(\vec{r}) \tag{12b}$$

Furthermore, the polarizability can be obtained from the asymptotic form of V^{Pa} as

$$\alpha(\hat{r}) = -2 \lim_{r \to \infty} r^4 V^{Pa}(\vec{r}) \tag{13}$$

where $\hat{r}$ is a unit vector indicating the direction from which the charge approaches. In practice one usually finds the limit by considering successively larger distances along an appropriate Cartesian axis, and $\hat{r}$ becomes a unit vector along that axis. We use the notation α_x, α_y and α_z for the polarizability components along the axes. In a similar fashion the dipole moment and the quadrupole moment of the unperturbed molecule can be obtained from the asymptotic form of V^S. For the specific case of H_2O, we obtain for the dipole moment

$$\mu = \lim_{z \to \infty} \frac{z^2}{2} [V^S(z) - V^S(-z)] \tag{14}$$

and for the quadrupole moments

$$\theta_{xx} = -\lim_{x \to \infty} x^3 V^S(x) \tag{15a}$$

$$\theta_{yy} = -\lim_{y \to \infty} y^3 V^S(y) \tag{15b}$$

$$\theta_{zz} = -\lim_{z \to \infty} \frac{z^3}{2} [V^S(z) + V^S(-z)] \tag{15c}$$

For these quantities the molecule is assumed to lie in the yz plane with the origin at the center of mass; the orientation is such that the oxygen is at $0.12413001\ a_0$ on the positive z axis and the hydrogens have a negative z component.

III.   CALCULATIONS AND BASIS SETS

Most calculations were carried out using a modified version of the computer program HONDO: Version 3,[9] although some were carried out using HONDO: Version 5.[10] As seen in equation (7), inclusion of the test charge simply adds a term to the one-electron portion of the total Hamiltonian. Thus, for a given set of internuclear coordinates, the two-electron integrals need only be computed once. We modified HONDO: Version 3 so that for each position $\vec{r}$ of the test charge (at a given molecular geometry), we simply recalculate

the one-electron integrals. The dominant amount of computer time is thus spent in iterating to self-consistency for various values of $\vec{r}$. We point out that convergence is sometimes quite slow especially if charge oscillations occur. The most difficult points to calculate in terms of charge oscillations are for values of $r < 2.0\ a_o$. Except for a few positions $\vec{r}$ (where no polarization potential is shown in the tables below) we were able to achieve convergence, although often up to 50 SCF iterations were needed. Although the program HONDO: Version 3 does not have efficient damping or extrapolation routines in the SCF algorithm, such routines are a valuable aid in determining polarization potentials. The program HONDO: Version 5 does have a more efficient convergence routine, and for the few calculations carried out with this program, a significant decrease in computer time was noted.

If the interaction potential is to be accurate at large r, it is necessary that the calculation yield accurate molecular polarizabilities and quadrupole moments. Polarizabilities can usually be calculated within 10-20% at the Hartree-Fock level, and dipole and quadrupole moments can often be calculated even more accurately. However, previous studies of polarizabilities have shown that large basis sets, including diffuse functions, are required in order to achieve this accuracy from a finite-field Hartree-fock approach.[1,11-13] In our previous work,[1,6,7] we found that good results could be obtained by placing the diffuse functions at the center of mass rather than on each nucleus. In other words we can treat the addition of polarizability-required diffuse functions in a similar way to Rydberg-state orbitals. This significantly lowers the number of basis functions required in these calculations.

The extended basis sets for water, neon and nitrogen are given in Table 1. The water basis was chosen as the culmination of an extensive study of the dependence of electron-water potentials on the basis sets; that study[14] will be published elsewhere. The basis set for H_2O may be labelled (12,8,3/7,1/1,1)/[8,7,3/6, 1/1,1] where the quantities in parenthesis are numbers of primitive functions and those in brackets are numbers of contracted functions, commas separate numbers of s, p and d functions on each center, and the centers are listed in the order O/H/center of bond. This basis set was obtained in the following manner. The starting basis for oxygen was the (10,6) primitive set of Huzinaga *et al.*[15] Only the first five s orbitals and the first two p orbitals were contracted. The s and p basis sets on oxygen were each augmented with two diffuse functions whose exponents were obtained by extending the two smallest exponents in the Huzinaga sets as geometric series. Two sets of diffuse d functions were also added at the oxygen to help describe the diffuse nature of the perturbed charge cloud. The starting s basis for H was the five-function primitive set of Huzinaga[16] and the first two orbitals were contracted. Two diffuse

Table 1. Large basis sets for H_2O, Ne and N_2

Molecule	Starting contracted basis[a]	Shell	Center	Exponent
				Additional basis functions
H_2O	(10,6/5)/[6,5/3]	S	O	0.084697561, 0.028051598
			H	0.0709526, 0.0223829
			B	1.265
		P	O	0.056438757, 0.019303615
			H	0.1
			B	0.569
		D	O	1.0, 0.23, 0.077
Final H_2O basis[a]		(12,8,3/7,1/1,1)/[8,7,3/6,1/1,1]		
N_2	(9,5)/[5,3]	S	N	0.065
			B	1.13, 0.27
		P	B	0.68, 0.19, 0.0515
		D	B	0.11
Basis 5 for N_2[a]		(10,5/2,3,1)/[6,3/2,3,1]		
N_2	basis 5	D	N	0.98
Basis 10 for N_2[a]		(10,5,1/2,3,1)/[6,3,1/2,3,1]		
Ne	(11,7)	S	Ne	0.11063952, 0.041541207
		P	Ne	0.081227922, 0.030593605
		D	Ne	2.72, 0.68, 0.227
Final Ne basis[a]		(13,9,3)		

[a] (XYZ/XY/ABC)/[xyz/xy/abc] means that there are X(x) primitive (contracted) S shells, Y(y) primitive (contracted) P shells and Z(z) primitive (contracted) D shells on each nucleus with oxygen preceding hydrogen and A (a) primitive (contracted) S shells, B (b) primitive (contracted) P shells and C (c) primitive (contracted) D shells at the bond midpoint.

s functions, with exponents obtained as described above for oxygen, and a diffuse p function, with exponent 0.1, were added to this H basis. An s orbital and a set of p orbitals were placed at the center of each O-H bond in order to describe the bond polarization effect. The exponents for the bond functions were optimized using the smaller basis $(10,6/4/1,1)/[5,3/2/1,1]$ with exponents and contraction coefficients for the O and H basis sets taken from Huzinaga $et\ al.$[15,16] A set of d functions with an exponent of 1.0 was added at the oxygen in order to help describe lone pair polarization. Since the center of mass is very close to the oxygen, no diffuse functions were added at this point as was done in our previous work[1,6,7] on homonuclear diatomics. The neon basis, $(13,9,3)$, is derived from the $(11,7)$ basis of Huzinaga $et\ al.$[15] As for oxygen, additional diffuse s and p exponents were obtained by a geometric expansion. The three d functions were taken from the work of Werner and Meyer.[11] The first basis shown for N_2 (basis 5 of reference 1) is of the form $(10,5/2,3,1)/[6,3/2,3,1]$. The nitrogen basis was obtained from the $(9,5)/[5,3]$ basis set used by Dunning[17] with a diffuse s function whose exponent was determined by geometric extension. Two s bond functions and two sets of p bond functions were added at the center of the bond (center of mass) to describe bond polarization as well as polarization by the incoming charge; and sets of diffuse p and d functions were added to describe the diffuse character of the perturbed wave function. The next basis shown for N_2, to be called basis 10, is discussed in section IV. The STO-3G basis sets were taken from the literature.[2]

For H_2O[18] and N_2,[19] the experimental geometries were employed. The geometric parameters are $r(O-H) = 1.811096\ a_0$ and $\theta(H-O-H) = 104.45°$ for H_2O and $r(N-N) = 2.068\ a_0$ for N_2. Calculations of the potentials for H_2O were carried out along the positive z, negative z, x and y axes as defined above. For N_2, calculations were carried out on the z axis and on the x axis, where the latter is the perpendicular bond bisector.

IV.   ENERGIES, POLARIZABILITIES AND PERMANENT MULTIPOLE MOMENTS

Our calculated values of the energies, polarizabilities and dipole and quadrupole moments for the basis sets considered in this chapter are summarized in Tables 2 - 4. In Tables 5 and 6, we compare the large-basis-set results for H_2O and N_2 with other work while the comparison for Ne is given in Table 3. The permanent multipole moments and the polarizability components govern the long-range asymptotic form of the static potential and adiabatic polarization potential, respectively; the long-range portions of these potentials are very important for scattering applications. Furthermore, the determination of these quantities allows us to determine the quality of our basis set and thus helps to provide an indication

Table 2. Properties of H_2O determined with a large
          basis set and an STO-3G basis set[a]

Property	Large basis	STO-3G	Experiment
E_o	-76.06091	-74.96312	---
I.P.[b]	13.86	10.64	12.614 (22)
μ	0.7850[c]	0.6771[c]	0.724 (24)
θ_{xx}	-1.8373[c]	-0.9750[c]	-1.86 (25)
θ_{yy}	1.9061[c]	0.9563[c]	1.96 (25)
θ_{zz}	-0.0708[c]	0.0008[c]	-0.10 (25)
α_x	7.914[c]	0.608[c]	---
α_y	9.203[c]	5.783[c]	---
α_z	8.492[c]	2.687[c]	---
α_0[d]	8.536[c]	3.026[c]	9.82 (11, 26)

[a] All values in atomic units (see preface of this book for conversion factors to other units) unless noted. Numbers in parentheses are reference numbers.

[b] Ionization potential from Koopmans' theorem (reference 21) in eV.

[c] Effective value at $r = 25\ a_o$.

[d] Spherical average of polarizability.

Table 3.   Total Energy and Polarizability for Ne[a]

Basis	Type of Calculation	Ref.	E_o	α
GTO (13, 9, 3)	HF SCF	c	−128.54494	2.367[b]
STO-3G	HF SCF	c	−126.60453	0.0
GTO (12, 8, 4)	HF SCF	12	---	2.368
GTO (12, 8, 4)	PNO-CI	12	---	2.618
GTO (12, 8, 4)	CEPA	12	---	2.676
(numerical)	HF SCF	33	---	2.377
STO	MCSCF	36	---	2.369
STO	CI	34	−128.6466	2.55
(experiment)		32	---	2.669

[a]All values in atomic units.
[b]Effective value at $r = 25\ a_o$.
[c]This work.

Table 4. Properties of N_2 determined with two large basis
sets and an STO-3G basis set[a]

Property	Basis 5	Basis 10	STO-3G	Experiment
E_o	-108.97325	-108.97742	-107.49493	---
IP^b	16.78	---	14.70	15.580 (23)
θ_{zz}	-0.974^c	---	-1.931^c	-1.04 ± 0.07 (37)
α_x	9.4^c	---	2.39^c	10.20 (39)
α_z	13.26^c	15.38^c	6.92^c	14.82 (39)
α_0^d	10.70^c	---	3.90^c	11.74 (39)
α_2^e	2.56^c	---	3.02^c	3.08 (39)

[a] All values in atomic units unless noted. Numbers in parentheses
are reference numbers.

[b] Ionization potential from Koopmans' theorem (reference 21) in eV.

[c] Effective value at $r = 15$ a_o.

[d] $\alpha_0 = (2\alpha_x + \alpha_z)/3$.

[e] $\alpha_2 = 2(\alpha_z - \alpha_x)/3$.

Table 5. Comparison of Various Properties for H_2O[a]

Basis	Type of Calculation	Ref.	E	μ	α_x	α_y	α_z	α_0
GTO (12,8,3/7,1/1,1)/[8,7,3/6,1/1,1]	HF SCF	b	−76.0609	0.785	7.91	9.20	8.49	8.50
GTO (10,6,2/4,1)/[5,3,2/2,1] (I)	HF SCF	20	−76.0326	0.802	7.84	9.09	8.34	8.42
GTO (10,6,2/4,1)/[5,3,2/2,1] (I)	RSMBPT 3	20	−76.2111	0.765	9.11	9.56	9.17	9.28
GTO (9,5,2/4,2)/[4,2,2/2,2] (K)	HF SCF	20	−76.0511	0.802	7.38	9.00	8.20	8.19
GTO (9,5,2/4,2)/[4,2,2/2,2] (K)	RSMBPT 3	20	−76.2756	0.752	8.38	9.52	8.94	8.95
GTO (9,5,2/4,2)/[4,2,2/2,2] (K)	CI	20	−76.2693	0.752	8.34	9.49	8.98	8.93
GTO [11,6,3/5,2]	HF SCF	11	−76.0553	0.782	7.99	9.04	8.47	8.50
GTO [11,6,3/5,2]	PNO-CI	11	−76.2152	0.739	9.95	9.17	9.45	9.52
GTO [11,6,3/5,2]	CEPA	11	−76.2246	0.782	10.14	9.66	9.79	9.86
GTO (13,8,2/8,2)/[7,5,2/4,2]	SCF	27	−76.0643	0.785	7.00	8.69	7.48	7.82
experiment		24,26		0.724				9.82

[a] All quantities in atomic units.

[b] This work.

of the accuracy of the interaction potentials even at short range. There has been a significant amount of previous work on the polarizabilities of H_2O and N_2. A summary of the water work has been provided by Zeiss *et al.*[20] while we have previously summarized the work on N_2.[1] We thus compare with only a selected set of previous calculations of polarizabilities for these molecules in Tables 3, 5 and 6. Tables 2 and 5 also compare ionization potentials calculated by Koopmans' theorem[21] to experimental values[22,23] for H_2O and N_2.

We compare our two calculations of the polarizability components of H_2O in Table 2. This table shows that the STO-3G basis is quite inadequate, especially for α_x which is at least an order of magnitude too small; of the three polarizability components, only α_y is within a factor of two of the result determined using the larger basis. The dipole moment and quadrupole moments determined with the minimum basis set are also smaller than those calculated with the large basis set. Tables 2 and 5 show that the dipole moment determined from the large basis set is in quite good agreement with experiment;[24] it is 8% too high. The quadrupole moments θ_{xx} and θ_{yy} also show excellent agreement with experiment;[25] θ_{zz} is too low by 21%, but this is a very small quantity and the absolute difference is small. The calculated value for α_0 is lower than experiment[11,26] by 13%. This kind of difference is in the typical range of 10-20% error for SCF-level calculations.

In Table 5, we compare our large-basis-set results with the large-basis-set results of Werner and Meyer,[11] Swanstrom *et al.*[27] and Zeiss *et al.*[20] Within the group compared, Swanstrom *et al.*[27] have obtained the lowest unperturbed energy but also the lowest, and hence worst, value for the polarizability. (Their good unperturbed energy results from a better treatment of the inner shell on the oxygen.) Zeiss *et al.*[20] used somewhat smaller basis sets with carefully chosen polarization functions and exponential scale factors. Their values for the polarizability components determined with their basis I are in good agreement with the best SCF results (reference 11 and this work), although the unperturbed energy for that basis is poor. Although basis K of these workers gives a better unperturbed energy, the polarizability components are quite low when compared with the best SCF results. Werner and Meyer's[11] HF SCF results and the ones reported here are in good agreement. We note that the calculated dipole moments are all somewhat high in comparison with experiment while the calculated polarizabilities are low. Such behavior is typical at the SCF level.

Werner and Meyer[11] and Zeiss *et al.*[20] also employed various correlation schemes in order to obtain estimates of the size of the correlation corrections to the polarizability. Werner and Meyer employed the pseudonatural-orbital configuration-interaction

(PNO-CI)[28] and coupled-electron-pairs approximation (CEPA)[29] methods while Zeiss *et al.*[20] performed configuration-interaction (CI) calculations[30] including single and double excitations and also performed calculations using Rayleigh-Schroedinger many-body perturbation theory (RSMBPT) up to third order.[31] As shown in Table 5, the correlated calculations of Zeiss *et al.*[20] with basis K account for less than 50% of the error between the SCF results and the experimental results. With the smaller basis I, somewhat better results are obtained. The CEPA results[11] are in good agreement with experiment while the PNO-CI results[11] give only 77% of the correlation correction. Werner and Meyer[11] also show that the values for the polarizability components and α_0 must be properly vibrationally averaged for accurate comparison with experiments; for water, this correction factor is about 2%.

For Ne, the STO-3G value for α is zero as compared to a value of 2.37 a_0^3 calculated with the large basis set. The value of zero for α at the STO-3G level arises because all of the orbitals that can be formed from a minimum basis set are occupied for this system; thus there is no variational freedom to provide polarization when the external field due to the impinging charge is applied. In comparison with experiment,[32] the value calculated for α_0 with the large basis set is 13% too low. Werner and Meyer[12] employed large basis sets and determined an SCF value consistent with our result. Our results are also in good agreement with those of Voegel *et al.*,[33] who used a numerical Hartree-Fock (HF) method.

Table 3 also contains the results of some Ne polarizability calculations including correlation. As for H_2O, the CEPA calculation of Werner and Meyer[12] gives good agreement with experiment. The CI calculation of Hibbert *et al.*[34] is based on a multiconfiguration self-consistent-field[35] (MCSCF) wave function with a large number of STO's. However, their value of the polarizability is not as close to experiment as the value obtained in the CEPA calculations. For smaller atoms, *e.g.* Be, the results of Hibbert *et al.*[34] and Werner and Meyer[12] show good agreement. It appears from these results and the results for H_2O that CEPA does account for most of the correlation energy needed to calculate accurate polarizabilities. Stevens and Billingsley[36] also determined the value of α from an MSCSF wave function, again using a large basis set of STO's. However, their value for α is the same as that determined for the Hartree-Fock limit. Thus, their calculations apparently do not account for correlation effects on the polarizability.

Table 4 shows that the STO-3G polarizabilities for N_2 are too small as compared to the values obtained with basis 5. The value for θ_{zz} at the minimum-basis-set level is too large (in contrast to the results for H_2O where the value for θ_{zz} is too small). The value determined with the large basis set for θ_{zz} is in good

agreement with experiment,[37] and with the numerical Hartree-Fock value of -0.940 a.u. determined by McCullough;[38] the values for α_x and α_z are smaller than the experimental[39] values. The value for α_z shows the largest error. Since we have previously[1] provided a detailed comparison of our results for N_2 with other determinations, Table 6 compares our values only with the best results and with new results. The best Hartree-Fock polarizabilities are those of Morrison and Hay[13] for α_z and α_x and the numerical Hartree-Fock determination of α_z by Christiansen and McCullough ($\alpha_z = 14.9\ a_0^3$).[40] These two values for α_z show good agreement with each other while our value for α_z is too small. In contrast, our value for α_x is in good agreement with the value of Morrison and Hay.[13] The main difference between our basis 5 and that of Morrison and Hay[13] is the presence of a set of tight nuclear-centered d functions in the latter set. (We showed previously[1] that the use of diffuse nuclear-centered d functions did not change the value of α_z significantly.) Based on this comparison and on our work on H_2O,[14] we concluded that we could obtain better results by adding a set of tight nuclear-centered d functions to our basis 5. Following Morrison and Hay,[13] we choose an exponent of 0.98 for these functions; the resulting basis set is called basis 10. This basis yields an unperturbed energy 0.003 E_h lower than the value of Morrison and Hay.[13] With basis 10, we calculated an effective α_z of 15.38 a_0^3 with the test charge at r = 15 a_0. To make very precise comparisons we must consider the difference between the effective value at 15 a_0 and the true limit of equation (13). Morrison and Hay[41] have compared effective values computed at 15 a_0 to limiting values where the latter were calculated using a uniform electric field. For α_z they showed that the effective value at 15 a_0 is higher by 4.7%. Scaling down our basis-10 value for α_z by a factor of 1.047 yields 14.68 a_0^3, which is in good agreement with the Hartree-Fock-limit value[40] of 14.9 a_0^3. This confirms that tight d functions at the nuclei are required for accurate calculations of α_z for N_2. A similar result was observed in the calculation of α_z for H_2O.[14]

It would be desirable for us to calculate the effective polarizabilities at even larger r values to eliminate the small correction mentioned in the last paragraph, but this is not always possible, at least with our programs. For example, we found that the difference between E_2 and E_1 gets so small that the limiting value of the polarizability is not approached in a numerically stable fashion if we consider r > 15 a_0 for N_2.

Correlation corrections for α_z and α_x are presumably small for N_2 since the Hartree-Fock values are quite good. Morrison and Hay[42] performed generalized-valence-bond[43] (GVB) calculations, splitting the three bond pairs with strong-orthogonality and perfect-pairing constraints, and they found a slight increase in

Table 6. Comparison of Polarizabilities for N_2[a]

Basis	Type of Calculation	Ref.	α_x	α_z	α_0	α_2
GTO (10,5/2,3,1)/[6,3/2,3,1] (5)	HF SCF	b	9.42[c]	13.26[c]	10.70[c]	2.56[c]
GTO (10,5,1/2,3,1)/[6,3,1/2,3,1] (10)	HF SCF	b	--	15.38[c]	--	--
GTO (10,6,2)/[6,4,2]	HF SCF	13	9.75	14.79	11.42	3.36
GTO (10,6,2)/[6,4,2]	GVB	42	9.81	13.64	11.10	2.55
GTO	HF SCF	44,45	9.93	15.15	11.67	3.48
GTO	PNO-CI	44,45	9.96	14.74	11.55	3.19
GTO	CEPA	44,45	10.02	14.54	11.55	2.99
numerical	HF	38	--	14.90	--	--
experiment		39	10.20	14.58	11.74	3.08

[a]Polarizabilities in atomic units.

[b]This work.

[c]Effective value at $r = 15\ a_0$.

α_x. However, the value for α_z showed a significant decrease (see Table 6). Thus correlation corrections at this level of approximation do not necessarily improve the results. This must be a consequence of an uneven treatment of correlation effects in the perturbed and unperturbed molecules. As discussed above, in conjunction with the use of a tight set of d orbitals to describe the lone pair, it is possible that the lone pairs must also be split in order to calculate a good value for α_z. Botschwina and Meyer[44,45] have determined correlation corrections at the CEPA level. Their value for α_z is low as compared to the Hartree-Fock value. This correlation correction is in the same direction as that determined from the GVB calculations. The Hartree-Fock value of Botschwina and Meyer[44,45] is actually above the value determined by the numerical Hartree-Fock calculations. Their value for α_x is in good agreement with our value and only a small correlation correction is found, increasing α_x. It is important to note that α_z actually decreases when correlation is included, reversing the usual trend.

A number of qualitative conclusions about accurate calculations of polarizabilities and, thus, about the long-range part of the interaction potential can now be made. The spherical average of the polarizability of a molecule can usually be roughly approximated as the sum of the atomic polarizabilities. Thus, in order to determine good molecular polarizabilities it is necessary to determine good atomic polarizabilities. As shown by a number of workers,[1,6,7,11-14,20] this requires good basis sets with both valence-polarization and diffuse functions. Similar basis sets will thus be needed for molecules. Since other nuclear centers are present with additional basis functions, their basis functions will help in polarizing the charge cloud and somewhat smaller basis sets on each atom may be employed. Although good agreement with experiment can often be obtained by optimizing a small basis set in order to obtain an optimum value for α_0, this can lead to a physically unreasonable wave function (this may account, for example, for the effect of configuration interaction on the value of α_0 for Li_2[46]). As shown for N_2 and H_2O, it is necessary to allow for the proper polarization near an atom by using tight functions as well as to allow for polarization of the entire charge cloud by using diffuse functions.

Quadrupole moments are somewhat easier to calculate and a good double-zeta-plus-polarization basis set is usually adequate for determining this static property.[47] (See reference 38 for a discussion of basis-set problems in determining quadrupole moments.)

Good polarizabilities (within 20%) and quadrupole moments can be obtained at the Hartree-Fock limit. In contrast, the values determined from an STO-3G basis usually show large errors. Polarizabilities are too low since there is not enough flexibility in the

basis. Quadrupole moments can be either high or low since they are
determined by a cancellation of two large terms. Since the long-
range form of the interaction potentials depends critically on these
quantities, significant errors can be introduced with the STO-3G
basis as shown below.

V.   INTERACTION POTENTIALS

    Figures 1-4 show that the polarization potentials for H_2O as
determined with the large basis set and the STO-3G basis set show
significant differences. The static potentials do not show as much
variation although there are still some significant differences for
certain directions of approach of the charge. The distance in the
figures is measured from the molecular center of mass. Since the
origin is very close to the oxygen, the static potential for $r < 1$ a_o
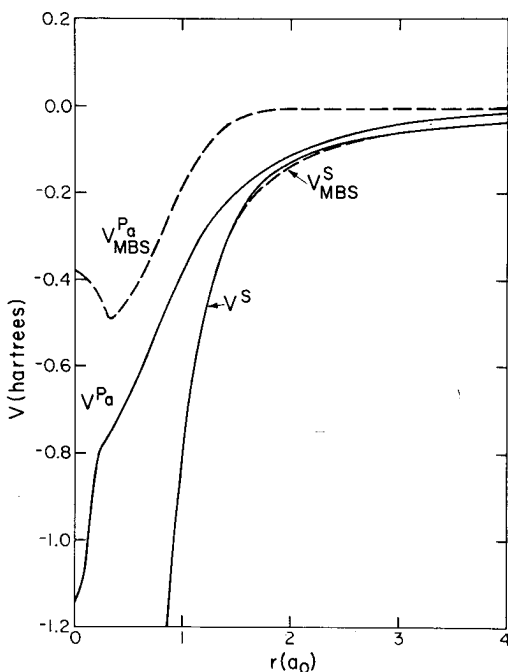
Figure 1.   Electron-H_2O interaction potentials for approach along
            the negative z axis. V^{Pa} is the adiabatic polarization
            potential, V^S is the static potential and MBS is an
            abbreviation for minimum basis set (STO-3G). Solid curves
            are employed for potentials determined with the large GTO
            basis, and dashed curves are employed for potentials
            determined with the STO-3G basis.

Figure 2. Same as Figure 1 except for approach along the positive
z axis.

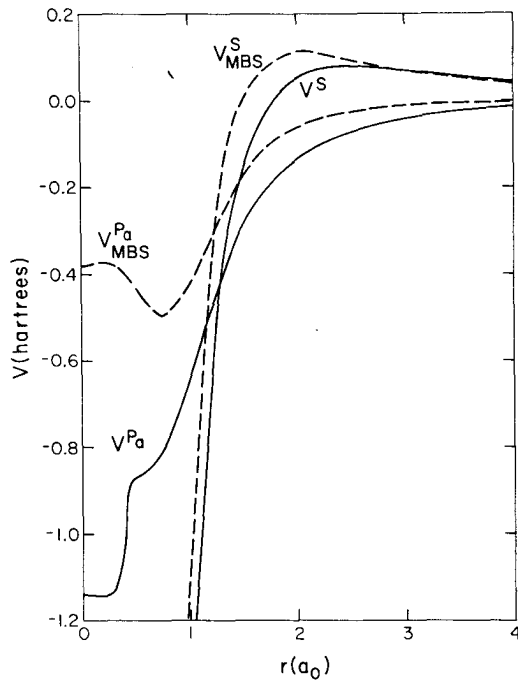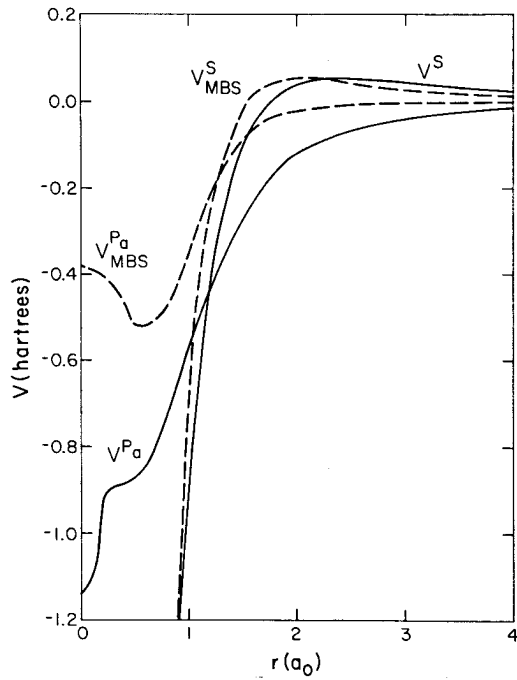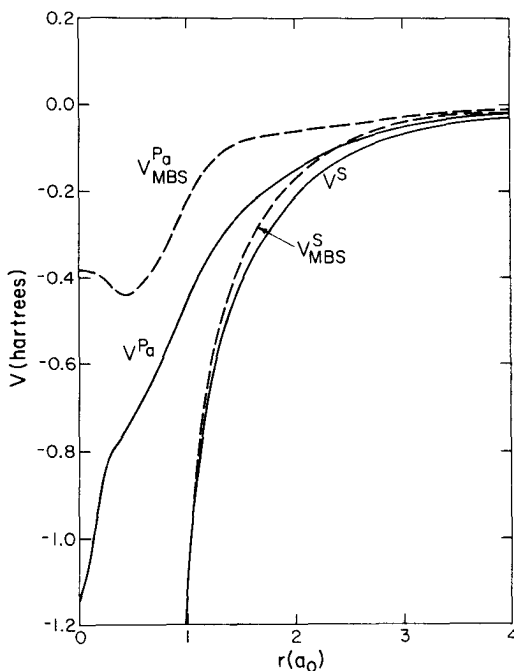Figure 3.   Same as Figure 1 except for approach along the x axis.

Figure 4. Same as Figure 1 except for approach along the y axis.

is dominated to a large extent by the interaction of the electron
and the oxygen nucleus. Thus, the effective potential there is
highly attractive. However, for larger distances, the ratio of the
static to the polarization potential depends strongly on the direc-
tion of approach.

On the negative z axis, the static potential at the STO-3G
level is in excellent agreement with the large-basis-set one out to
4 a_o. At larger distances, due to errors in the STO-3G quadrupole
moment, the difference between the two calculations of V^S becomes
significant. Along the positive z axis the two calculations of V^S
differ significantly in the region of 1-2 a_o. The static potential
obtained using the minimum basis set shows more repulsive character
in this region than does the one from the large-basis-set calcula-
tions, and it falls off more slowly. Along the x axis, the static
potentials differ in a similar fashion except that at larger r the
STO-3G calculation underestimates the static potential. Along the
y axis, the static potentials are similar with the one determined
from the large basis set always falling below the value for the
minimum basis set.

The x and positive z directions of approach correspond to the
negative charge impinging on the lone pairs. In these regions, the
basis set must be very flexible. The minimum basis leads to a bump
in the static potential for these directions of approach. In con-
trast, the large basis set shows more polarization and no pronounced
bump. Thus, in these regions, the static potential provides a good
test of basis-set adequacy. A similar result is found for the charge
approaching along the y axis where it probes the portion of the OH
bond near the oxygen. Approaching along the negative z axis, the
charge does not probe any major electron distribution, and the
static potential in this direction shows the least difference between
the two basis sets.

The forms of the polarization potentials for $r < 2$ a_o are
strongly influenced by their values at the origin. Since the minimum
basis set yields much too small a value at the origin, the forms of
the potential determined from the two basis sets are quite different
in the whole small-r region. The minimum basis set yields -0.38 E_h
for V^{Pa} $(r = 0)$ as compared to the large-basis-set value of -1.14 E_h.
The polarization potential determined from the minimum basis set
shows a minimum between 0.25 and 0.75 a_o for each of the four
directions of approach. In contrast the large-basis-set polariza-
tion potential is most attractive at the origin or at the oxygen.
Instead of a minimum it shows only a kink between 0.25 and 0.75 a_o.
Along the y and negative z axes, the kink is simply a rapid change
of slope. Along the positive z and x axes, there is a suggestion
of a secondary minimum. These two directions of approach correspond
to the lone-pair directions, as already discussed.

Of course, it is the full potential, V^{SPa} (the sum of V^S and
V^{Pa}), that governs the motion of the approaching charge in the
adiabatic approximation. Table 7 shows that the full interaction
potentials show significant differences between the two basis sets.
Along the x axis the full interaction potentials have different
signs at $r = 2.0$ a_o, where the large basis set yields an attractive
potential while the STO-3G basis set yields net repulsion. Along
this axis, the potential barrier is 1.02 eV at the STO-3G level,
but it is only 0.24 eV with the large basis. In this direction,
the large-basis-set potential dies off much more slowly at large r
than the STO-3G one does, and it is dominated by the static poten-
tial. Along the y axis the general form of the two potentials is
similar although V^{SPa} determined from the large basis set is
significantly more attractive. Along the positive z axis, the
total interaction potential determined with the large basis has a
smaller repulsive maximum (0.85 eV) located at larger r than does
the corresponding potential determined with the STO-3G basis (the
latter has a maximum of 1.88 eV). Again the STO-3G potential dies
off more rapidly. As for the y axis, the accurate potential along
the negative z axis is always attractive, and it is significantly

Table 7. Static and polarization potentials (in E_h)
          calculated with the two basis sets for H_2O

r (a_o)	Large basis V^S V^{SPa}	V^{Pa}	STO–3G V^S V^{SPa}	V^{Pa}
Along x axis				
0.00	−46.246396 −47.384153	−1.137757	−46.328420 −46.709135	−0.380715
0.20	−19.475177 −20.402287	−0.927110	--- ---	---
0.25	−15.186408 −16.087456	−0.901048	−15.195577 −15.607300	−0.411723
0.50	−5.352596 −6.224922	−0.872326	−5.236602 −5.752584	−0.515982
0.75	−2.156021 −2.918044	−0.762022	−1.967762 −2.458883	−0.491121
0.90	−1.263207 −1.912589	−0.649382	--- ---	---
1.00	−0.880172 −1.446783	−0.566611	−0.691436 −1.035622	−0.344186
1.25	−0.336512 ---	---	−0.193583 −0.381160	−0.187576
1.50	−0.100896 ---	---	−0.013918 −0.101695	−0.087776
1.90	0.027944 −0.107359	−0.135303	--- ---	---
2.00	0.039373 −0.079911	−0.119284	0.053831 0.033995	−0.019836
2.50	0.053241 −0.013907	−0.067148	0.043074 0.037170	−0.005904
3.00	0.043884 0.004140	−0.039744	0.028918 0.026714	−0.002204
3.50	0.032929 0.008654	−0.024275	0.019394 0.018429	−0.000965
4.00	0.024235 0.008976	−0.015258	0.013462 0.012989	−0.000474
5.00	0.013454 0.006870	−0.006584	0.007185 0.007040	−0.000145
6.00	0.008026 0.004833	−0.003193	0.004256 0.004201	−0.000055
8.00	0.003478 0.002478	−0.001001	0.001840 0.001827	−0.000013
10.00	0.001803 0.001397	−0.000406	0.000953 0.000949	−0.000004

Table 7. Continued.

r (a_o)	Large basis V^S V^{Spa}	V^{Pa}	STO-3G V^S V^{SPa}	V^{Pa}

Along x axis (continued)

r (a_o)	V^S / V^{Spa}	V^{Pa}	V^S / V^{SPa}	V^{Pa}
15.00	0.000541 / 0.000462	−0.000079	0.000286 / 0.000285	−0.000001
20.00	0.000229 / 0.000204	−0.000025	0.000121 / 0.000121	−0.000000
25.00	0.000118 / 0.000107	−0.000010	0.000062 / 0.000062	−0.000000
30.00	--- / ---	---	0.000036 / 0.000036	−0.000000

Along y axis

r (a_o)	V^S / V^{Spa}	V^{Pa}	V^S / V^{SPa}	V^{Pa}
0.00	−46.246396 / −47.384153	−1.137757	−46.328420 / −46.709135	−0.380715
0.25	−15.250021 / −16.089341	−0.839320	−15.315872 / −15.723207	−0.407334
0.50	−5.491131 / −6.217203	−0.726072	−5.528493 / −5.962795	−0.434302
0.75	−2.342163 / −2.942457	−0.600294	−2.339328 / −2.695028	−0.355700
1.00	−1.112565 / −1.564458	−0.451893	−1.082997 / −1.308307	−0.225310
1.25	−0.615498 / −0.946558	−0.331059	−0.575458 / −0.703318	−0.127860
1.50	−0.404533 / −0.654484	−0.249951	−0.362190 / −0.446930	−0.084740
2.00	−0.216071 / −0.367408	−0.151337	−0.174593 / −0.237665	−0.063072
2.50	−0.117198 / −0.205989	−0.088791	−0.081618 / −0.126827	−0.045209
3.00	−0.067326 / −0.118577	−0.051251	−0.040580 / −0.068936	−0.028356
3.50	−0.042108 / −0.072355	−0.030247	−0.023077 / −0.040185	−0.017108
4.00	−0.028261 / −0.046757	−0.018497	−0.014699 / −0.025178	−0.010479
5.00	−0.014692 / −0.022429	−0.007736	−0.007366 / −0.011731	−0.004365
6.00	−0.008616 / −0.012326	−0.003710	−0.004309 / −0.006401	−0.002092

Table 7.   Continued.

r (a$_o$)	Large basis		STO-3G	
	V^S V^{SPa}	V^{Pa}	V^S_{SPa}	V^{Pa}

Along y axis (continued)

8.00	-0.003680 -0.004837	-0.001156	-0.001848 -0.002501	-0.000653
10.00	-0.001894 -0.002363	-0.000469	-0.000952 -0.001218	-0.000266
15.00	-0.000564 -0.000655	-0.000092	-0.000284 -0.000336	-0.000052
20.00	-0.000238 -0.000267	-0.000029	-0.000120 -0.000136	-0.000017
25.00	-0.000122 -0.000134	-0.000012	-0.000061 -0.000068	-0.000007
30.00	--- ---	---	-0.000035 -0.000039	-0.000004

Along z axis

0.00	-46.246396 -47.384152	-1.137757	-46.328420 -46.709135	-0.380715
0.25	-45.390720 -46.531124	-1.140404	-45.391358 -45.765469	-0.374111
0.50	-9.426526 -10.296147	-0.869622	-9.302346 -9.732702	-0.430356
0.75	-3.432799 -4.238691	-0.805892	-3.196480 -3.693250	-0.496770
1.00	-1.351360 -1.987562	-0.636201	-1.086661 -1.510333	-0.423672
1.25	-0.513155 -0.955223	-0.442068	-0.285975 -0.576267	-0.290292
1.50	-0.159233 -0.448136	-0.288903	0.003694 0.171861	-0.175555
1.80	0.008098 -0.174146	-0.182244	--- ---	---
1.90	0.034318 -0.123490	-0.157808	--- ---	---
2.00	0.052208 -0.085284	-0.137493	0.112862 0.051323	-0.061539
2.50	0.078395 0.004561	-0.073834	0.094291 0.068810	-0.025481
3.00	0.069298 0.026975	-0.042323	0.069750 0.057410	-0.012349

Table 7.   Continued

| r (a_o) | Large basis | | STO-3G | |
	V^S V^{SPa}	V^{Pa}	V^S V^{SPa}	V^{Pa}
Along z axis (continued)				
3.50	0.056177 0.030944	-0.025233	0.052238 0.045533	-0.006705
4.00	0.045050 0.029452	-0.015598	0.040393 0.036432	-0.003961
5.00	0.029950 0.023309	-0.006641	0.026192 0.024545	-0.001647
6.00	0.021132 0.017906	-0.003225	0.018345 0.017541	-0.000804
8.00	0.012075 0.011054	-0.001022	0.010422 0.010164	-0.000258
10.00	0.007788 0.007370	-0.000418	0.006705 0.006599	-0.000107
15.00	0.003488 0.003406	-0.000083	0.002998 0.002977	-0.000021
20.00	0.001967 0.001941	-0.000026	0.001691 0.001633	-0.000007
25.00	0.001260 0.001250	-0.000011	0.001083 0.001080	-0.000003
30.00	--- ---	---	0.000753 0.000751	-0.000002
-0.25	-9.712298 -10.498288	-0.785990	-9.801987 -10.255491	-0.453504
-0.50	-3.755975 -4.430784	-0.674809	-3.818804 -4.262848	-0.444044
-0.75	-1.668551 -2.196528	-0.527977	-1.702893 -2.029349	-0.326456
-1.00	-0.808485 -1.189148	-0.380663	-0.826270 -1.010672	-0.184402
-1.25	-0.431871 -0.699703	-0.267832	-0.445822 -0.525572	-0.079750
-1.50	-0.258685 -0.452749	-0.194065	-0.272472 -0.300034	-0.027562
-2.00	-0.127027 -0.238825	-0.111798	-0.136996 -0.142168	-0.005171
-2.50	-0.081966 -0.148703	-0.066737	-0.086763 -0.091833	-0.005071
-3.00	-0.060464 -0.101025	-0.040561	-0.062127 -0.066709	-0.004582

Table 7.   Continued.

r (a_o)	Large basis V^S V^{Spa}	V^{Pa}	STO-3G V^S V^{SPa}	V^{Pa}
-3.50	-0.047478 -0.072692	-0.025214	-0.047442 -0.050930	-0.003488
-4.00	-0.038553 -0.054612	-0.016059	-0.037557 -0.040050	-0.002492
-5.00	-0.026883 -0.033929	-0.007046	-0.025168 -0.026419	-0.001251
-6.00	-0.019637 -0.023086	-0.003449	-0.017938 -0.018604	-0.000666
-8.00	-0.011599 -0.012685	-0.001087	-0.010337 -0.010568	-0.000231
-10.00	-0.007584 -0.008025	-0.000441	-0.006684 -0.006782	-0.000099
-15.00	-0.003440 -0.003526	-0.000086	-0.002998 -0.003018	-0.000021
-20.00	-0.001949 -0.001976	-0.000027	-0.001691 -0.001698	-0.000007
-25.00	-0.001251 -0.001262	-0.000011	-0.001083 -0.001086	-0.000003
-30.00	--- ---	---	-0.000753 -0.000754	-0.000002

deeper than found using the minimum basis set. As before, the static term provides the dominant portion of the interaction energy at large r.

For the neon atom, Table 8 and Figure 5 show that the STO-3G static potential is everywhere less attractive than the one calculated with the large basis set. This effect is similar to that observed for an electron approaching H_2O in the negative z direction. The fact that the small basis set allows for no polarization term for neon makes the differences in V^{SPa} larger than those in V^S. The V^{VPa} term predicted by the large basis set for neon is quite different from that for water; Ne has a minimum in V^{Pa} at r = 0.3 a_o, in contrast to the inflection points found in the H_2O potentials. The values of V^{Pa} with the elctron at the origin are similar for H_2O and Ne, which is not surprising since they are isoelectronic. The total interaction potential of Ne is dominated by V^{Pa} for r > 1.5 a.u. Thus the STO-3G prediction of V^{SPa} is much shorter in range than the potential obtained with the large basis set.

Table 8.   Static and polarization potentials (in E_h)
            calculated with the two basis sets for Ne

| r (a_o)	Large Basis			STO-3G
	V^S	V^{Pa}	V^{SPa}	V^S
0.01	−969.005488	−1.0002	−971.0057	−969.31319
0.25	−21.097979	−1.07072	−22.16870	−21.022735
0.5	−5.959645	−0.9045	−6.8641	−5.684910
0.75	−2.093433	−0.564724	−2.658157	−1.768186
1.0	−0.803076	−0.302472	−1.105548	−0.549062
1.25	−0.326186	−0.177586	−0.503771	−0.170024
1.5	−0.138188	−0.115505	−0.253693	−0.052461
2.0	−0.027368	−0.053849	−0.081217	−0.004262
2.5	−0.005925	−0.026836	−0.032762	−0.000223
3.0	−0.001349	−0.014238	−0.015587	−0.000007
3.5	−0.000308	−0.008001	−0.008309	−0.000001
4.0	−0.000068	−0.004751	−0.004819	0.0
5.0	−0.000004	−0.001943	−0.001947	0.0
6.0	−0.000001	−0.000931	−0.000932	0.0
8.0	0.0	−0.000292	−0.000292	0.0
10.0	0.0	−0.000119	−0.000119	0.0
15.0	0.0	−0.000023	−0.000023	0.0
20.0	0.0	−0.000007	−0.000007	0.0
25.0	0.0	−0.000003	−0.000003	0.0
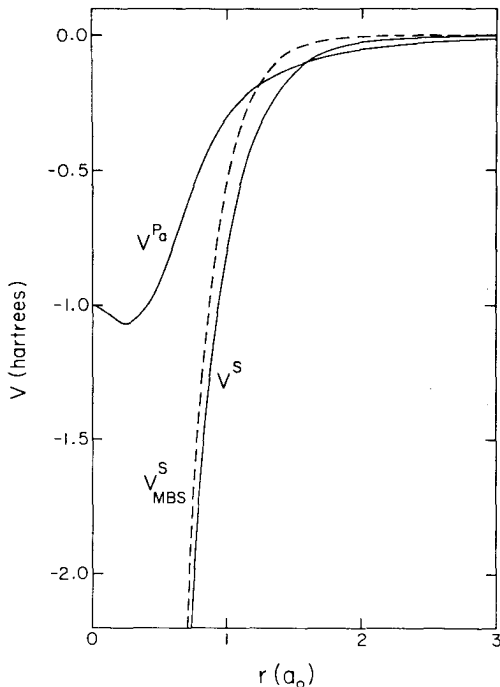
Figure 5.   Same as Figure 1 except for electron–Ne interaction
             potentials.

        The minimum-basis-set static potential for N_2 shows defici-
encies for both the perpendicular (x axis) and parallel (z axis)
approaches (see Table 9 and Figures 6 and 7).   For perpendicular
approach, both static potentials are attractive at all r, but the
STO-3G one is always too strong, especially near the origin.   For
parallel approach, however, the STO-3G static potential is signifi-
cantly more repulsive than the potential from basis set 5 at large
r.   This is due to the error in the value of θ at the STO-3G level.
For N_2, the polarization potentials do not even show comparable
forms.   The STO-3G basis predicts negligible polarization at the
origin whereas V^{SPa} is 26% more attractive than V^S for basis set 5.
For the perpendicular approach, the STO-3G polarization potential
is extremely flat, in marked contrast to the large-basis-set
result.   The STO-3G polarization potential for the parallel approach
has qualitatively the same form as the large-basis-set result, but
it is too small by a factor of 3.5 at small r.   This factor decreases
to 1.9 at r = 2.5 a_o, then increases to 2.6 at 4-5 a_o, and decreases
to 1.9 at 15 a_o.

Table 9. Static and polarization potentials (in E_h) calculated with the two basis sets for N_2

r (a_o)	Basis 5			STO-3G		
	V^S V^{SPa}	V^{Pa}		V^S V^{SPa}	V^{Pa}	

Along x axis

r (a_o)	V^S / V^{SPa}	V^{Pa}	V^S / V^{SPa}	V^{Pa}
0.01	−1.885810 / −2.366791	−0.480981	−2.175388 / −2.188619	−0.013231
0.5	−1.375634 / −1.785746	−0.410112	−1.564001 / −1.585373	−0.021372
0.75	−0.973982 / −1.315571	−0.341589	−1.084587 / −1.111685	−0.027098
1.25	−0.403053 / −0.610501	−0.207448	−0.424819 / −0.454820	−0.030001
1.5	−0.248456 / −0.406484	−0.158028	−0.257711 / −0.285104	−0.027393
2.0	−0.094799 / −0.190227	−0.095428	−0.100978 / −0.120518	−0.019541
2.5	−0.038896 / −0.099103	−0.060207	−0.046978 / −0.059623	−0.012645
3.0	−0.017833 / −0.056184	−0.038351	−0.026640 / −0.034636	−0.007996
3.5	−0.009428 / −0.033977	−0.024549	−0.017408 / −0.022519	−0.005111
4.0	−0.005817 / −0.021713	−0.015896	−0.012243 / −0.015590	−0.003347
5.0	−0.003026 / −0.010127	−0.007101	−0.006726 / −0.008289	−0.001562
15.0	−0.000138 / −0.000231	−0.000093	−0.000280 / −0.000303	−0.000024

Along z axis

r (a_o)	V^S / V^{SPa}	V^{Pa}	V^S / V^{SPa}	V^{Pa}
0.5	−5.022004 / −5.5606	−0.5385	−5.270908 / −5.424026	−0.153118
0.75	−13.460554 / −14.0746	−0.6140	−13.645436 / −13.844871	−0.199435
1.25	−19.685189 / −20.4079	−0.7227	−19.731954 / −19.996864	−0.264910
1.5	−6.109009 / −6.7811	−0.6720	−6.085104 / −6.352162	−0.267058
2.0	−1.152380 / −1.6253	−0.4729	−1.005118 / −1.229505	−0.224388

Table 9. Continued.

r (a_0)	Basis 5		STO-3G	
	V^S V^{SPa}	V^{Pa}	V^S V^{SPa}	V^{Pa}

Along z axis (continued)

r (a_0)	V^S	V^{Pa}	V^S	V^{Pa}
2.5	-0.227756	-0.2320	-0.097777	-0.119722
	-0.4598		-0.217498	
3.0	-0.027627	-0.1192	0.045553	-0.055320
	-0.1469		-0.009767	
3.5	0.012373	-0.0675	0.050159	-0.027572
	-0.0552		0.022587	
4.0	0.016296	-0.0396	0.036927	-0.015277
	-0.0234		0.021650	
5.0	0.009949	-0.0155	0.018179	-0.005894
	-0.0056		0.012285	
15.0	0.000295	-0.000131	0.000578	-0.000068
	0.000164		0.000510	

The total interaction potential for N_2, as determined with basis set 5, is dominated by the polarization potential from r = 2 a_0 to beyond r = 5 a_0 for perpendicular approach and for r = 2.5-10 a_0 for parallel approach. The interaction potential at the STO-3G level, however, is dominated by the static potential at all r for both directions of approach except near the zero of V^S for parallel approach. As a consequence, the two calculations of V^{SPa} differ considerably, especially for parallel approach. In particular, for z = 3-5 a_0, the STO-3G static-plus-adiabatic polarization potential is repulsive whereas the basis-5 one is attractive. Since the STO-3G static potential is too attractive for perpendicular approach, there is some cancellation of errors in the two contributions to V^{SPa} for this direction of approach.

A further reduction in rigor and computational costs below the minimum-basis-set level is achieved by treating only the valence electrons and introducing neglect-of-differential overlap approximations. A popular minimum-basis-set method incorporating such approximations is the INDO method.[48] To calculate static potentials, it is useful to add non-polarizable localized atomic core orbitals; this yields the INDO/1s method.[49] In calculating one-electron properties by this method, the standard practice is to retain one-center differential overlap contributions. An alternative way to calculate one-electron properties from INDO wave functions leads to the INDOXI/1s method where the XI stands for excluding
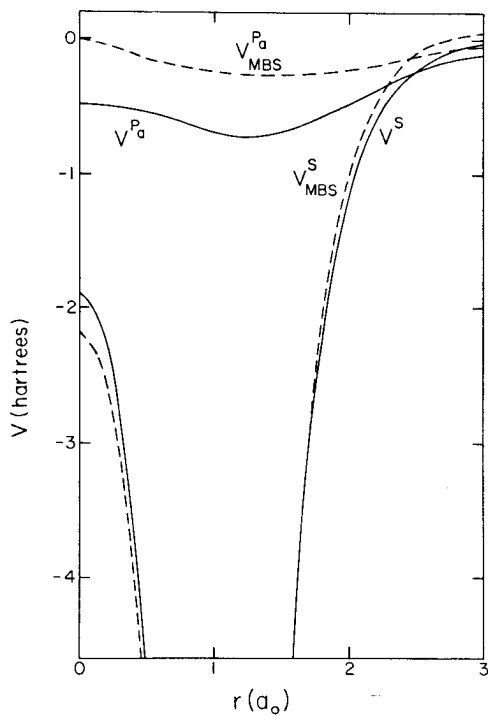
Figure 6.   Electron-N_2 interaction potentials for approach along
the z axis.   Solid curves are for basis 5 and dashed
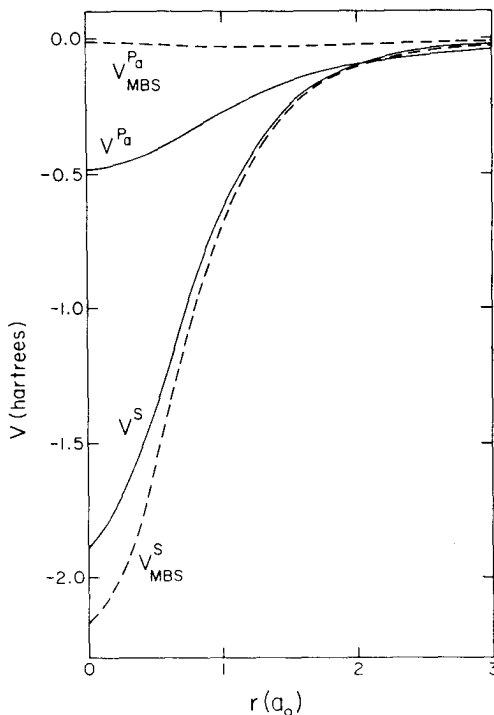curves are for STO-3G.

Figure 7.   Electron-N_2 interaction potentials for approach along
            the x axis.   Solid curves are for basis 5 and dashed
            curves are for STO-3G.

intraatomic differential overlap in calculating the one-electron
property.[49]   Both of these methods have been applied to calculating
static potentials and polarization potentials for electron scatter-
ing[49-59] and the static potentials have been compared to large-
basis-set results for N_2 and CO and to a (95)/[21] minimum-basis-set
calculation for N_2.[49,50]   We have seen previously[1,54,56,58,59] that
these methods underestimate the polarization potential as compared
to basis 5.   Here we can compare the INDO and INDOXI calculations
of V^{Pa} to the STO-3G potentials.   At the origin all three minimum-
basis set methods give very small values of V^{Pa}:   -0.0065 E_h for
INDO, -0.0135 E_h for INDO/1s, and -0.0132 E_h for INDOXI.   Moving
away from the origin along the x axis, the INDO and STO-3G polari-
zation potentials are very similar for x = 1-5 a_o while the INDOXI
one is smaller by factors increasing from 3 to 10^2 over this range.
Along the z axis the INDOXI and STO-3G values are very similar for
z = 1-5 a_o.   The INDO calculation of V^{Pa} is in good agreement with
INDOXI for z = 0.5 - 1 a_o, becomes a factor of 2 more attractive at
2 a_o, and then becomes similar again for z = 3-5 a_o.   Thus the

semiempirical minimum-basis-set calculations underestimate the amount
of charge polarization just as *ab initio* minimum-basis-set calcula-
tions do.

It has been suggested[59] that the use of a minimum basis set in
calculating the adiabatic polarization potential at small r may be
a reasonable way to simulate a nonadiabatic polarization potential
for electron scattering at low or intermediate impact energies.
The justification of this is that the minimum basis set excludes
"distant" regions of the target Hilbert space which are inaccessible
during rapid passage of the electron. This justification is only
approximate, and it is more valid for some targets than for others.
For example, this model cannot be applied to neon for which the
minimum-basis-set polarization potential is zero. For molecular
targets, this model for the nonadiabatic polarization potential can
be and has been tested by comparing scattering calculations to
experiment as reviewed in the previous chapter in this book. For
heavy-body interactions in chemistry, for example proton-molecule
interactions, the nonadiabatic corrections are not important. In
such cases the use of minimum basis sets to calculate polarization
effects always leads to a serious systematic underestimation of
such effects.

The orbital-eigenvalue spectrum provides a measure of the
quality of an SCF wave function and the region in which it will be
valid. In Table 10 we summarize the eigenvalue spectrum for H_2O
with the test charge at the origin, at $z = 2.0$ a_o, and at infinity
with both basis sets. The large basis set yields five negative
orbital eigenvalues for all three positions of the test charge and
in fact for every position of the test charge that we examined.
Thus the ten original electrons of water can all be accommodated in
bound orbitals. Even with the test charge at the origin the
highest occupied molecular orbital is bound by 1.22 eV. As we
have shown before,[1,6,7] this destabilization of the charge distri-
bution with an electron at the molecular origin is typical. However,
this energetic destabilization with the electron at the origin is
more than compensated by the large attractive interaction of the
electron with the various nuclei. In the large-basis-set calcula-
tion, the incoming charge causes a switch in the ordering of the
orbitals with the $3a_1$ orbital becoming the highest occupied
molecular orbital when the test charge is at the origin. In con-
trast, the $1b_1$ orbital is the highest with no test charge present.
The STO-3G results are quite different. With the test charge at
the origin, there are two positive eigenvalues and another eigen-
value is only barely negative. With the test charge at $z = 2.0$ a_o,
there is still one positive eigenvalue. Apparently the minimum
basis set does not have enough flexibility to allow the original
electrons to all remain bound if a negative test charge is brought
too close. Other work[60] has shown that if positive eigenvalues are

Table 10.   Comparison of eigenvalues in eV for H_2O perturbed
            by an electron on the symmetry axis

z (a_o)	∞	2.0	0.0
	Large basis		
ε_1	-559.58 (a_1)	-552.27 (a_1)	-437.54 (a_1)
ε_2	-36.81 (a_1)	-27.93 (a_1)	-22.76 (a_1)
ε_3	-19.52 (b_2)	-10.98 (b_2)	-8.61 (b_2)
ε_4	-15.90 (a_1)	-5.07 (b_1)	-3.29 (b_1)
ε_5	-13.86 (b_1)	-2.96 (a_1)	-1.22 (a_1)
	STO-3G basis		
ε_1	-550.78 (a_1)	-542.71 (a_1)	-415.29 (a_1)
ε_2	-34.50 (a_1)	-25.15 (a_1)	-12.75 (a_1)
ε_3	-16.79 (b_2)	-7.42 (b_2)	-0.23 (b_2)
ε_4	-12.33 (a_1)	-0.85 (b_1)	7.01 (a_1)
ε_5	-10.64 (b_1)	2.51 (a_1)	10.49 (b_1)

present at the conclusion of an SCF calculation, care must be taken
in analyzing the wave function.

The orbital-eigenvalue spectrum of N_2 with a test charge at
its origin (or at $x = 0.01$ a_o for the large basis set) is compared
to the unperturbed orbital-eigenvalue spectrum in Table 11.   The
minimum basis set leads to three unbound occupied orbitals with
the test charge at the origin.   In contrast, with the large basis
set all occupied orbitals are bound by at least 2.4 eV.

V.   CONCLUDING REMARKS

Static potentials for reactivity predictions are often
determined with a minimum basis (usually STO-3G).   A stated con-
clusion from a number of these studies[61,62] is that the polariza-
tion potential is often small in comparison to the static potential.
As illustrated for N_2 and Ne in this chapter, the latter result may
be obtained with STO-3G calculations even when the polarization

Table 11.   Comparison of eigenvalues in eV for N_2 perturbed
            by an electron on the perpendicular bisector

x (a_o)	Basis 5		STO-3G	
	∞	0.01	∞	0.0
ε_1	−426.91	−415.39	−422.28	−396.15
ε_2	−426.82	−415.33	−422.22	−396.09
ε_3	−40.27	−21.89	−39.34	−13.52
ε_4	−21.15	−11.84	−19.65	−4.90
ε_5	−17.25	−5.21	−15.65	3.47
ε_6	−16.78	−5.21	−15.65	3.47
ε_7	−16.78	−2.42	−14.70	7.55

potential is the dominant term at intermediate r in a more accurate
calculation.   In a previous study on Li_2,[7] for approach on the x
axis (defined as for N_2), the polarization potential was found to
be twice as large as the static potential.   Even though the polari-
zation potential is smaller than the static potential for H_2O, it
cannot be neglected in determining the net interaction potential.
Indeed, V^{Pa} significantly reduces the repulsive nature of V^S for some
directions of approach in that case.   Although the interaction poten-
tials determined with the two basis sets, for example for approach
along x for H_2O, may be similar, this is caused by a cancellation
of errors since V^S is too large and V^{Pa} is too small.   The minimum
basis set always yields polarizabilities that are too small and
thus V^{Pa} will always be too small at large r.   This led previous
workers to conclude, incorrectly, that V^{Pa} can be ignored relative
to V^S.   Since V^S may actually be too large at the minimum basis set
level (for example, because of an incorrect determination of θ),
this can reinforce the incorrect conclusion.   Thus, significant
care must be used when attempting to describe the interaction of
charges with atoms and molecules in terms of only the static
potential.   In the case of electron scattering, the fortuitous
cancellation of errors in V^S and V^{Pa} that sometimes occurs is not
as helpful as for heavy-particle interactions.   The reason is that
this fortuitous cancellation can disappear when nonadiabatic
corrections are employed.

     Results from small basis sets are important in providing
qualitative and even semiquantitative information about molecular
interactions.   However, our quantitative comparisons showed that

minimum-basis-set static potentials may be significantly in error, especially at large r, and that minimum-basis-set polarization potentials are uniformly too small. Further studies with large basis sets are needed for comparison and calibration purposes.

VI.   ACKNOWLEDGMENTS

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