PHYSICAL REVIEW A VOLUME 20, NUMBER 3 SEPTEMBER 1979

Ab initio self-consistent-field polarizabilities and electron-molecule adiabatic polarization potentials. III. N_2

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(Received 29 January 1979)

Electric dipole polarizabilities and electron-molecule static and adiabatic polarization potentials are calculated by means of *ab initio* molecular-orbital theory. Nine different basis sets involving 18–48 contracted Gaussian basis functions are used. The authors show that bond-centered basis functions are very efficient for polarizability calculations: a 46-function calculation yields a spherically averaged polarizability α_0 within (6–7)% of the 56-function calculation of Morrison and Hay and the 76-function calculation of Schneider. As compared to Schneider's calculation, 18 functions underestimate α_0 by 39% and two 26-function calculations underestimate it by 26% and 31%. These small basis sets may be useful for qualitative purposes, but the results show that the adiabatic polarization potentials at small electron-molecule distances are not less sensitive than polarizabilities to basis-set variations and truncations. Full adiabatic polarization potentials are reported for both 18-function and 47-function basis sets.

I. INTRODUCTION

This paper presents a study of the static electric dipole polarizability and the adiabatic polarization potential (APP) for electron scattering for the molecule N_2 at the self-consistent-field molecular-orbital level using the finite-field approach in which the molecular wave function is variationally optimized in the presence of a negative test charge. In earlier papers in this series we have presented *ab initio* self-consistent-field (SCF) molecular-orbital calculations of the static electric dipole polarizabilities and adiabatic electron-scattering polarization potentials for H_2 (Ref. 1) and Li_2.[2] There are several previous *ab initio* calculations of the electric-dipole polarizabilities of N_2.[3-13] Early calculations used perturbation theory[3-5,8,9]; finite-field approaches, like the present one, have been applied to this problem more recently.[6,7,10-13] There has been only one *ab initio* study of the electron-scattering adiabatic polarization potential for electron scattering by N_2 (Ref. 14); it is not yet published, but the emphasis is on large electron-molecule separations.[15] Our emphasis is on smaller electron-molecule separations. Gready, Bacskay, and Hush[12] have examined the interactions of N_2 and CO with whole and fractional positive charges and with charge patterns representative of crystal surfaces. These studies are complementary to the present study involving a negative test charge, but although the electrostatic interactions of single test charges with unperturbed molecules are just proportional to the perturbing charge, when adiabatic relaxation is included the results for positive and negative perturbers are no longer related by a sign change.

Since N_2 contains two atoms from the important C-N-O group, it may be considered a prototype for many other molecules of interest, e.g., O_2, C_2H_2, CO, NO, CO_2, N_2O. For this reason we report an extensive study of basis-set variations employing contracted Gaussian-type functions and including both large and small bases; we hope the conclusions about what levels of accuracy are attainable with different size bases will be applicable to both polarizability calculations and scattering calculations for other similar systems. In order to treat the problem accurately, the basis set must be sufficiently complete to account for not only the charge-density difference between isolated atoms and a molecule (bond polarization of the atomic densities) but also the pertrubation of the molecular charge density by the perturbing test charge. We have tested a variety of augmented double zeta-basis sets and focus on the use of bond-centered functions[16] to describe both the bond polarization and the polarization of the diffuse portion of the total charge distribution induced by the negative charge. (Bond-centered functions are basis functions positioned on the axis joining two nuclei but not centered at either of the nuclei.) We also discuss the use and limitations of very simple basis sets derived from the standard STO-3G (Ref. 17) and 4-31G (Ref. 18) basis sets proposed by Pople and collaborators. The former basis set consists of two *s* functions and one *p* function on each nuclear center; the latter consists of three *s* functions and two *p* functions on each center. We augment both basis sets with bond-centered functions.

The motivation for the present studies is the use of the adiabatic polarization potentials as one step in the development and understanding of realistic optical potentials for calculations of electron scattering cross sections.[19,20] Scattering calculations using approximations to the adiabatic polarization potential based on the intermediate neglect of differential overlap (INDO) and intermediate neglect of differential overlap without intra-atomic terms

(INDOXI) semiempirical molecular-orbital approximations[20] have already been carried out, and the calculated differential cross sections[21] are in qualitative agreement with experimental[22] results. However, the present results show that the accurate adiabatic polarization potential is significantly more attractive than the INDO and INDOXI approximations to it. Since the polarization potential at large electron-molecule separations is determined by the static electric-dipole polarizability, we compare the present calculations of this quantity to experimental and previous theoretical results in order to test the adequacy of various basis sets and to develop schemes for constructing computationally efficient basis sets for future work on polyatomic molecules. Finally we study the orbital energies of the target molecule as perturbed by the scattering electron at various locations in order to develop a better physical picture of the detailed response of the target during a collision.

II. THEORY AND CALCULATIONAL DETAILS

The theoretical approach is the same as described elsewhere.[1,10,12] Briefly, the procedure is as follows. Given a one-electron basis set, we perform a self-consistent-field molecular-orbital calculation on the isolated molecule to obtain the zero-field energy E_0. Then the electrostatic interaction with a fixed test charge (of charge -1) is added to the molecular Hamiltonian and the molecular orbitals are reoptimized to self-consistency in the presence of the test charge. The initial and final energies in these new self-consistent-field iterations correspond to the original unperturbed molecular orbitals and fully relaxed molecular orbitals, respectively, and we denote these energies E_1 and E_2. The location of the test charge is specified by its distance r from the center of the molecule and the angle χ between the molecular axis and a vector from the center of the molecule to the test charge. The static potential V^S, the adiabatically polarized potential V^{SP_a}, and the adiabatic polarization potential V^{P_a} are defined for a given internuclear distance R by

$$V^S(r,\chi,R)=E_1(r,\chi,R)-E_0(R)\,, \tag{1}$$

$$V^{SP_a}(r,\chi,R)=E_2(r,\chi,R)-E_0(R)\,, \tag{2}$$

$$V^{P_a}(r,\chi,R)=V^{SP_a}(r,\chi,R)-V^S(r,\chi,R)\,, \tag{3}$$

and effective electric dipole polarizabilities

TABLE I. Basis sets.

Basis	Starting contracted basis set	Shell	Additional basis functions Center	a_k	Whole basis set Composition[a]	Size[b]
1	(95)/[53]	S	B	1.13, 0.30, 0.07		
		P	B	0.68, 0.07, 0.03	(95/33)/[53/33]	40
2	(95)/[53]	S	B	1.13, 0.30, 0.07		
		P	B	0.68, 0.24, 0.08, 0.03	(95/34)/[53/34]	43
3	(95)/[53]	S	B	1.13, 0.30, 0.07		
		P	N	0.0515		
			B	0.68, 0.24, 0.08	(96/33)/[54/33]	46
4	(95)/[53]	S	B	1.13, 0.27, 0.065		
		P	B	0.68, 0.19, 0.0515		
		D	B	0.11	(95/331)/[53/331]	46
5	(95)/[53]	S	N	0.065		
			B	1.13, 0.27		
		P	B	0.68, 0.19, 0.0515		
		D	B	0.11	(10 5/231)/[63/231]	47
6	(95)/[53]	S	B	1.13, 0.065		
		P	B	0.68, 0.0515		
		D	N	0.16	(951/22)/[531/22]	48
7	STO-3G	L	B	0.9, 0.1	(63/22)/[21/22]	18
8	STO-3-21G	L	B	0.9, 0.1	(63/22)/[32/22]	26
9	4-31G	L	B	0.9, 0.1	(84/22)/[32/22]	26

[a] $(XYZ/ABC)/[xyz/abc]$ 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 and $A(a)$ primitive (contracted) S shells, $B(b)$ primitive (contracted) P shells, and $C(c)$ primitive (contracted) D shells at the bond midpoint.

[b] Size is the total number of contracted functions.

$\alpha(r,\chi,R)$ and and effective electric quadrupole moment $\theta(r,\chi,R)$ are defined by

$$\alpha(r,\chi,R) = -2r^4 V^{P_\alpha}(r,\chi,R) \tag{4}$$

and

$$\theta(r,R) = -(\tfrac{2}{3}r^3)\left[V^S(r,0^\circ,R) - V^S(r,90^\circ,R)\right]\,. \tag{5}$$

The actual static electric-dipole polarizabilities $\alpha(\chi)$ and the electric-quadrupole moment θ are the $(r\rightarrow\infty)$ limits of these quantities. (Note that an alternative definition of the electric-quadrupole moment $Q=2\theta$ is sometimes used.) Finally, the isotropic and anisotropic components of the static electric dipole polarizability tensor are defined as $\alpha_0=\frac{1}{3}(\alpha_\parallel+2\alpha_\perp)$ and $\alpha_2=\frac{2}{3}(\alpha_\parallel-\alpha_\perp)$, where $\alpha_\parallel=\alpha(0^\circ)$ and $\alpha_\perp=\alpha(90^\circ)$.

The calculations were performed using the "HONDO 76: closed-shell Gaussian" computer program.[23,24] All calculations were done at the experimental internuclear distance for N_2, $2.068a_0$. [$1a_0 = 1$ bohr $= 0.529\,177\,06\times10^{-10}$ m; we use hartree atomic units (a.u.) in this paper.] We employed nine different basis sets which are summarized in Table I. The first six basis sets consist of a Huzinaga-Dunning (95)/[53] contracted Gaussian set[25,26] augmented by additional uncontracted Gaussian functions. In the notation of Ref. 23, the additional functions were S, P, or D shells with exponential parameters a_k and were either nuclear-centered (N) or centered at the bond midpoint (B). An S shell is a 1s Gaussian function, a P shell is a set of three 2p Gaussian functions, an L shell is an S shell and a P shell with the same orbital exponent, and a D shell is a set of one 3s and five 3d Gaussian functions. Details of the additional functions are given in Table I. The motivations for choosing these particular functions will be given in Sec. III. Bases 7–9 consist entirely of S and L shells, again using the notation of Ref. 23. Basis set 7 is the widely used STO-3G basis[17] augmented by two L shells at the bond midpoint. Basis set 8 is the same except the valence L shell of the STO-3G set is contracted into two functions instead of one (the functions with exponential parameter 0.285 715 are left uncontracted). Basis set 9 is the same as 7 except that the 4-31G basis set[18] replaces the STO-3G set.

III. RESULTS AND DISCUSSION

The zero-field energies and quadrupole moments for all nine bases are summarized in Table II where they are compared to other theoretical determinations[7,11,12,16,26-33] and the experimental value.[34] Basis 5 yields a very good energy for a Gaussian basis; the only basis sets in Table II that yield better energies are the Morrison-Hay basis and the basis sets composed of Slater-type

TABLE II. Zero-field properties.

Basis	E_0 (a.u.)	θ (a.u.)	Ref.
1	−108.971 01	−1.18[a]	b
2	−108.972 99	−1.03[a]	b
3	−108.973 04	−1.05[a]	b
4	−108.973 11	−0.976[a]	b
5	−108.973 25	−0.974[a]	b
6	−108.972 07	−0.961[a]	b
7	−107.634 37	−1.41[a]	b
8	−107.682 41	−0.911[a]	b
9	−108.817 87	−0.911[a]	b
Dunning (95)/[43][c]	−108.887 7	−1.79	26
Dunning (95)/[53]	−108.889 0	−1.79	26, 27
Gready-Bacskay-Hush (10 61)/[541]	−108.906 16	−1.15	7, 12
Vladimiroff (95/11)/[43/11]	−108.964 4	−1.25	16
Dunning (951)/[431]	−108.966 6	−1.245	28
Dunning (952)/[432]	−108.973 2	−0.992	27, 28
Morrison-Hay (10 62)/[642]	−108.974 2	−0.897	11
Nesbet	−108.971 43	−0.886	29
Cade-Sales-Wahl	−108.992 8	−0.947	30, 31
Hartree-Fock limit	−108.993 9	−0.940	32
MCSCF calculation[d]		−0.91	33
Experimental value		−1.04 ± 0.07	34

[a] Effective value at $15a_0$.

[b] This work.

[c] See footnote a in Table I.

[d] Multiconfiguration self-consistent-field calculation.

TABLE III. Effective polarizabilities.

	$\alpha(r,\chi)$ (a.u.)		
	$r=10a_0$	$15a_0$	$25a_0$
$\chi=0°$			
Basis 1	14.8	12.6	
Basis 2	15.5	13.2	
Morrison and Hay (Ref. 11)	16.4	15.5	15.1
$\chi=90°$			
Basis 1	6.7	6.7	
Basis 2	7.0	7.0	
Morrison and Hay (Ref. 11)	9.8	9.8	9.7

orbitals. We also note that basis 1 which contains three sets of s and p bond functions gives an excellent energy as compared to a (951)/[431] basis and gives almost as good an energy as a (952)/[432] basis. It thus appears that multiple-bond functions can span the space very well, and, based on the energetic criterion, they improve the description of the bond polarization. The results for the quadrupole moment provide an even better test for the need for additional functions to adequately describe the molecular charge distribution. For example, basis 4 includes a set of diffuse d functions at the center and it yields a more accurate quadrupole moment than bases 1–3. We also note a marked improvement in the quadrupole moment in going from basis 1 to basis 2 with the inclusion of a tighter p bond function. Thus for a good description of the molecular quadrupole, it is necessary to have a flexible enough basis set.

Table III presents effective polarizabilities calculated at $10a_0$ and $15a_0$ with basis sets 1 and 2. Table III shows that $\alpha_\perp$ is converged with respect to increasing r by these distances but that $\alpha_\parallel$ converges more slowly. However, the calculations of Morrison and Hay indicate that $\alpha_\parallel$ at $15a_0$ is only 3% larger than at $25a_0$. We considered this deviation acceptable so we calculated the effective polarizability at $15a_0$ for the other basis sets. We note that a similar problem occurs in finite-field approaches using uniform fields proportional to Fx and Fy, where F is the field strength and x and y are Cartesian coordinates. In such calculations the results should be converged with respect to decreasing F.

Table IV presents the effective polarizabilities at $15a_0$ for all nine basis sets and compares these results to other determinations including the ex-

TABLE IV. Electric-dipole polarizabilities (a.u.).[a]

	$\alpha_\parallel$	$\alpha_\perp$	α_0	α_2
Finite-field calculation				
Basis 1	12.6	6.7	8.6	3.9
Basis 2	13.2	7.0	9.1	4.1
Basis 3	13.4	7.1	9.2	4.2
Basis 4	13.4	9.3	10.7	2.7
Basis 5	13.3	9.4	10.7	2.6
Basis 6	13.2	9.7	10.9	2.3
Basis 7	9.5	5.2	6.6	2.9
Basis 8	12.2	6.6	8.5	3.8
Basis 9	11.1	6.3	7.9	3.2
Gutschick-McKoy (Ref. 6)	15.0	9.5	11.3	3.7
Gready-Bacskay-Hush (Refs. 7, 12)	14.5	9.5	11.2	3.3
Schneider (Ref. 10)	14.9	9.7	11.5	3.5
Morrison and Hay (Ref. 11)	14.8	9.7	11.4	3.4
Perturbation theory				
Kolker-Karplus (Ref. 3)	31.5	8.6	16.2	15.3
O'Hare-Hurst (Ref. 4)	27.3	13.2	17.9	9.4
Sinfailam-Thompson (Ref. 5)	16.6	11.7	13.3	3.3
Lamanna-Guidotti-Arrighini (Ref. 8)	13.2	8.2	9.9	3.3
Experiment				
Bridge and Buckingham (Ref. 35)[b]	15.1	10.4	11.9	3.1
Zeiss and Meath (Refs. 35, 37)[c]	14.82	10.20	11.74	3.08

[a] Present calculations are effective values at $15a_0$; Schneider's are effective values at $20a_0$.

[b] See Ref. 36.

[c] These values are obtained by combining the most accurate available α_0, from Ref. 37, with α_2 from Bridge and Buckingham (Ref. 35).

TABLE V. Interaction potentials (a.u.) for e^{-}-N_2 at $\chi = 0°$.

r (a_0)	Basis 1	Basis 2	Basis 5	Basis 7
0.50			−5.022 [a]	−5.259
			−0.539 [b]	−0.409
			−5.561 [c]	−5.667
0.75			−13.461	−13.716
			−0.614	−0.441
			−14.075	−14.156
1.25			−19.685	−19.886
			−0.723	−0.531
			−20.408	−20.417
1.50	−6.108		−6.109	−6.249
	−0.668		−0.672	−0.572
	−6.776		−6.781	−6.821
2.00		−1.151	−1.152	−1.147
		−0.453	−0.473	−0.448
		−1.604	−1.625	−1.595
2.50			−0.228	−0.182
			−0.232	−0.190
			−0.460	−0.371
3.00			−0.0276	0.0034
			−0.1192	−0.0762
			−0.1469	−0.0729
3.50			0.0124	0.0291
			−0.0675	−0.0387
			−0.0552	−0.0096
4.00			0.0163	0.0256
			−0.0396	−0.0225
			−0.0234	0.0032
5.00			0.0099	0.0136
			−0.0155	−0.0089
			−0.0056	0.0047
10.00	0.00124	0.00110		
	−0.00074	−0.00078		
	0.00050	0.00032		
15.00	0.00035	0.00031	0.00029	0.00042
	−0.00012	−0.00013	−0.00013	−0.00009
	0.00023	0.00018	0.00016	0.00033

[a] Top entry is static potential $V^{S}(r, \chi)$.

[b] Middle entry is adiabatic polarization potential $V^{P_a}(r, \chi)$.

[c] Bottom entry is adiabatically polarized potential $V^{SP_a}(r, \chi)$.

perimental values.[35-37] Tables V and VI and Figs. 1–3 present our calculations of the adiabatic polarization potentials for parallel and perpendicular-bisector approaches for five of the bases. Table VII presents a few calculations for other angles of approach.

The first striking feature of Table IV is the much greater reliability of the finite-field results over the perturbation-theory results. The difficulties of obtaining accurate results with perturbation-theory calculations using inexact zero-field wave functions have been stressed by Gutschick and McKoy.[6]

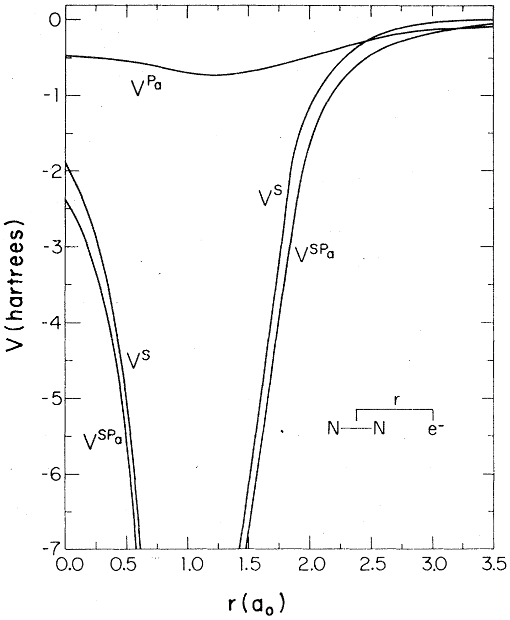

FIG. 1. Electron-N_2 interaction potentials for collinear approach calculated with basis 5.

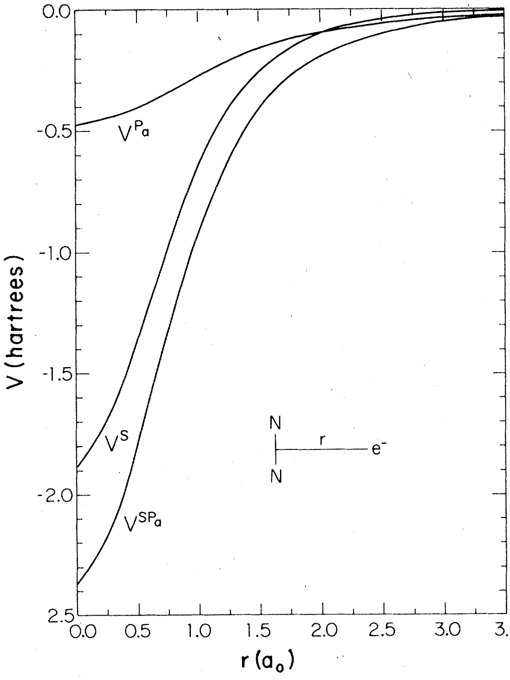

FIG. 2. Electron-N_2 interaction potentials for perpendicular-bisector approach calculated with basis 5.

TABLE VI. Interaction potentials (a.u.) for e^{-}-N_2 at $\chi = 90°$.

r (a_0)	Basis 1	Basis 2	Basis 5	Basis 7	Basis 8
0.01			−1.886 [a]	−2.076	−2.003
			−0.481 [b]	−0.383	−0.423
			−2.367 [c]	−2.459	−2.425
0.25				−1.904	
				−0.389	
				−2.293	
0.50			−1.376	−1.492	−1.447
			−0.410	−0.383	−0.400
			−1.786	−1.874	−1.847
0.75			−0.974	−1.039	−1.017
			−0.342	−0.333	−0.342
			−1.316	−1.373	−1.359
1.25			−0.403	−0.427	−0.431
			−0.207	−0.170	−0.188
			−0.611	−0.597	−0.619
1.50	−0.254		−0.248	−0.270	−0.278
	−0.141		−0.158	−0.110	−0.132
	−0.394		−0.406	−0.381	−0.410
2.00	−0.101 9	−0.094 1	−0.094 8	−0.115 3	−0.120 3
	−0.075 9	−0.083 7	−0.095 4	−0.053 2	−0.070 8
	−0.176 9	−0.177 8	−0.190 2	−0.168 5	−0.191 1
2.50	−0.044 0		−0.038 9	−0.053 8	−0.054 7
	−0.045 0		−0.060 2	−0.031 6	−0.041 7
	−0.089 0		−0.099 1	−0.085 4	−0.096 4
3.00			−0.017 8	−0.027 6	−0.026 2
			−0.038 4	−0.020 3	−0.026 0
			−0.056 2	−0.047 9	−0.052 3
3.50			−0.009 43	−0.015 78	−0.013 66
			−0.024 55	−0.013 24	−0.016 81
			−0.033 98	−0.029 02	−0.030 47
4.00			−0.005 82	−0.009 96	−0.007 83
			−0.015 90	−0.008 72	−0.011 07
			−0.021 71	−0.018 68	−0.018 90
5.00			−0.003 03	−0.004 92	−0.003 40
			−0.007 10	−0.003 97	−0.005 05
			−0.010 13	−0.008 89	−0.008 45
10.00	−0.000 56	−0.000 48			
	−0.000 33	−0.000 35			
	−0.000 89	−0.000 83			
15.00	−0.000 17	−0.000 15	−0.000 14	−0.000 20	−0.000 13
	−0.000 07	−0.000 07	−0.000 09	−0.000 05	−0.000 07
	−0.000 24	−0.000 22	−0.000 23	−0.000 25	−0.000 20

[a] Top entry is static potential $V^{S}(r, \chi)$.
[b] Middle entry is adiabatic polarization potential $V^{Pa}(r, \chi)$.
[c] Bottom entry is adiabatically polarized potential $V^{SPa}(r, \chi)$.

Table IV provides a useful guide as to what kinds of basis functions are necessary and sufficient for various levels of accuracy for the parallel and perpendicular polarizabilities. Before we consider our basis sets in order we first consider the previous finite-field SCF calculations. Gready, Bacskay, and Hush[7] took their basis from Gutschick and McKoy,[6] who augmented a Huzinaga-Dunning (95)/[43] set with nuclear-centered s, p, and d sets with exponents 0.08, 0.08, and 0.2. These added functions are all diffuse functions whose inclusion was motivated by the fact that they are

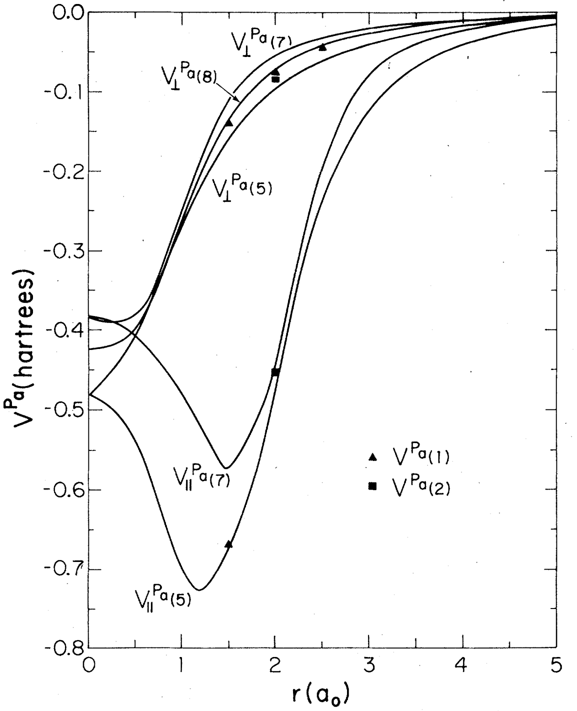

FIG. 3. Electron-N_2 adiabatic polarization potentials for collinear and perpendicular-bisector approaches calculated with several bases.

needed for adequate representation of the perturbed orbitals. They can be called diffuse polarization functions. This basis does not contain bond-polarization functions, such as nuclear-centered *d* functions with larger exponents or bond-centered *s* or *p* functions with larger exponents. Such bond-polarization functions are necessary for a good description of the unperturbed wave function (see the previous discussion). Nevertheless the added functions do improve the zero-field properties considerably (see Table II) and this basis set yields good polarizabilities. A safer approach is to begin with a basis already containing good bond-polarization functions and to augment it with diffuse polarization functions. Schneider[10] and Morrison and Hay[11] took this approach by starting with Huzinaga-Dunning (951)/[631] and (951)/[531] bases, respectively, and adding diffuse functions to improve the polarizability. Schneider added many such functions and optimized them for the atomic polarizability. A similar approach was applied successfully to first row hydrides by Werner and Meyer.[38] Morrison and Hay were able to get good results for N_2 with only one extra *S*, *P*, and *D* shell at each nucleus. They determined the exponential parameters of the added *S* and *P* shells by applying a geometric series extension to the two smallest *S* exponential parameters (0.7 and 0.2133) and the two smallest *P* exponential parameters (0.5314 and 0.1654) in the Huzinaga (95) set yielding 0.065 and 0.0515, respectively. Essentially following a suggestion of Werner and Meyer,[38] who were generalizing about the exponential parameters they optimized for polarizability calculations on a series of first-row hydrides such as NH_3, Morrison and Hay set the exponential parameter of their added *D* shell equal to the smallest *P* exponential parameter (0.1654) in the Huzinaga (95) set.

TABLE VII. Adiabatic polarization potential (a.u.) for e^--N_2 with basis 5 at $r = 2.0a_0$.

χ (deg)	Calculated	Predicted ($\lambda_{\max}^P = 2$)[a]	Error (%)
0	−0.4729	−0.4729	⋯
43.954 94	−0.2757	−0.2910	5.6
73.646 93	−0.1157	−0.1253	8.3
90	−0.0954	−0.0954	⋯

[a] $V^{Pa} \cong -0.2213 - 0.2516\, P_2(\cos\chi)$ determined from calculations at $\chi = 0°$ and $90°$.

Bases 1–5 and 7–9 represent our attempt to include both bond-polarization functions and diffuse polarization functions without using nuclear-centered *D* shells. The reason we try to avoid nuclear-centered *d* functions is economy. As explained above, a *D* shell contains six functions so using nuclear-centered *D* shells for both bond polarization and diffuse polarization effects requires 24 functions. The Schneider and Morrison-Hay calculations used 5-function *d* sets rather than 6-function *D* shells. Even so, using nuclear-centered *d* sets led to quite large basis sets. E.g., the Schneider calculation involved 82 contracted functions and the Morrison-Hay calculation involved 60 contracted functions; calculations with that many functions require very time-consuming self-consistent-field iterations. In contrast none of the basis sets 1–5 and 7–9 which avoid nuclear-centered *d* sets involves more than 47 contracted functions while the Gready-Bacskay-Hush basis and our basis 6, both of which use nuclear-centered diffuse *d* functions but no nuclear-centered bond-polarization functions, involve 46 and 48 functions, respectively. Since we do represent bond-polarization effects reasonably well we expect our polarizabilities to converge from below.

Basis 1 involves only 40 contracted functions. In this basis bond polarization is accounted for by the Vladimiroff[16] bond-centered *S* and *P* shells with exponential parameters 1.13 and 0.68, respectively. One diffuse *S* shell, two diffuse *P* shells, and a "filler" *S* shell are also added at the bond midpoint. The filler *S* shell has an exponential parameter which is roughly the geometric mean of the other two. Our motivation in putting the diffuse functions at the bond midpoint is that the spatial extent of these functions is so great that placing separate functions at each nucleus should be largely redundant. Tables II and IV show that, presumably because of the filler S shell, this calculation considerably improves Vladimiroff's E_0, but θ and the polarizabilities are still rather inaccurate.

Basis 2 is like basis 1 except that a filler P shell is added at the bond midpoint. This considerably improves θ, and $\alpha_\parallel$ and $\alpha_\perp$ increase by about 5%.

Basis 3 is like basis 2 except that the exponential parameter of the most diffuse P shell is raised to 0.0515 and this P shell is moved to the nuclei, which adds three more functions. The zero-field properties are essentially unaffected by this, but $\alpha_\parallel$ and $\alpha_\perp$ are improved very slightly. This confirms our belief that the calculations are not sensitive to the precise values of the exponential parameters or origins of the diffuse functions.

In basis 4 we used three S and P shells (one S and P for bond polarization, one diffuse S and P, and one S and P "filler") at the bond midpoint and one D shell at the bond midpoint. The exponent for the D shell is the polarizability-optimized value of Werner and Meyer for NH_3.[38] Inclusion of this D shell considerably improves the perpendicular polarizability, bringing it within 3% of the values found by previous workers[10,11] with larger basis sets.

Basis 5 is identical to basis 4 except that the most diffuse S shell is moved to the nuclei. This has a negligible effect, confirming that, just as for diffuse P shells, no accuracy is lost by centering these diffuse polarization functions at the bond midpoint.

Basis 6 is identical to basis 4 except the filler S and P shells are dropped and the D shell is moved out to the nuclei and given the Morrison-Hay exponential parameter. Now $\alpha_\perp$ is essentially identical to their value but $\alpha_\parallel$ is still not improved. It is difficult to understand why the Gready-Bacskay-Hush and Morrison-Hay bases give more accurate values than basis 6 for $\alpha_\parallel$.

Basis 7 is an attempt to be as economical as possible consistent with inclusion of bond-polarization functions and diffuse functions. Basis 7 augments an STO-3G minimum basis set with one bond-centered L shell for bond polarization and one diffuse bond-centered L shell. The exponential parameter 0.9 is the mean of Vladimiroff's optimized values of 1.13 and 0.68. The exponential parameter 0.1 for the diffuse functions is determined by the geometric mean extension of the two smallest exponential parameters (0.878 495 and 0.285 715) of the STO-3G primitive set. E_0 for basis 7 (as well as bases 8 and 9) is poor because the inner shell is not well represented, but that may be unimportant for polarizability calculations. For basis 7, θ, $\alpha_\parallel$, and $\alpha_\perp$ are all much worse than for bases 1–6. It should be pointed out though that basis 7 is much more accurate than the semiempirical molecular-orbital method INDO which yields $\theta = -3.17$ a.u. (Ref. 27) and $\alpha_\parallel = 7.0$ a.u., $\alpha_\perp = 2.6$ a.u. (Ref. 20). Yet, like INDO, the STO-3G method, even augmented with two L shells at the bond midpoint, would be economical enough to apply even to moderately sized polyatomic molecules at a number of geometries.

In basis 8, the outermost valence L shell of the STO-3G calculation is uncontracted. This considerably improves θ, $\alpha_\parallel$, and $\alpha_\perp$. An STO-3-21G-type basis without additional bond-centered functions has been applied to calculate the polarizability of ethylene by Mulder *et al.*[39]

Basis 9, the 4-31G basis, is an attempt to retain the physics included in basis 8 but to treat the inner shell more accurately. Disappointingly, although θ is hardly changed, $\alpha_\parallel$ and $\alpha_\perp$ are 9% and 5% worse, respectively.

We can draw several conclusions: (i) There is no loss in accuracy in centering diffuse s, p, and d functions at the bond midpoint; (ii) bond-centered functions provide a more economical way to include bond-polarization effects than do nuclear-centered functions; (iii) diffuse d functions as well as diffuse s and p functions are required for accurate calculations of $\alpha_\perp$; (iv) it is hard to converge $\alpha_\parallel$ to better than 10% accuracy without using very large basis sets; and (v) small-basis-set *ab initio* calculations underestimate the polarizability by on the order of 30% and are sensitive to the exact choice of functions, but they are significantly more accurate than the semiempirical INDO method. These results also suggest that diffuse bond-centered functions would be useful for calculations on Rydberg states or on negative ions where significant diffuse character is needed to properly describe the state.

Next we consider the interaction potentials for electron-molecule scattering. We selected basis 5, which yields the best zero-field energy of the nine bases tried for our most accurate calculations. Since it yields the lowest E_0, it is least likely to overestimate the adiabatic polarization potential due to basis set deficiencies. Further the static potential computed with this basis set is in excellent agreement with that computed earlier[27] for the (952)/[432] basis. The interaction potentials calculated with basis 5 are shown in Figs. 1 and 2.

Table V and Fig. 1 show that for collinear approach of the electron the static potential greatly dominates the adiabatic polarization potential within $0.5a_0$ of the nuclei (the nuclei are at $r=1.034a_0$). At $r=2.0a_0$, V^S still exceeds V^{Pa} by a factor of 2.5. At $1.5a_0$ and $2.0a_0$ the test we performed with augmented double-zeta bases showed that the value for V^{Pa} at these distances is less sensitive to the choice of set than is the value for $\alpha_\parallel$ (see Table V and Fig. 3). We computed $V^{Pa}(r, \chi=0°)$ over the whole range of r for both bases 5 and 7. As compared to basis 5, basis 7 underestimates $\alpha_\parallel$ by 28%. In the range $1.5-2.5a_0$, it underestimates V^{Pa} by 18% or less, as compared to basis 5, but at both smaller and larger r the relative differences in V^{Pa} are comparable to or larger than in $\alpha_\parallel$. Thus adiabatic polarization potentials do not seem to be less sensitive to basis-set variations at small and medium r than at large r.

Next consider the center of the molecule. Table VI includes a point $0.01a_0$ from the center of the molecule. The adiabatic polarization potential there is calculated to be −0.38 to −0.48 a.u., depending on method. This is an appreciable contribution and is much larger than calculated previously by the INDO method.[20] Since the adiabatic polarization potential is not negligible at the center of the molecule, it will be important to study nonadiabatic effects, which may be important there (as they are known to be important in electron-atom collisions[40-51]). In particular, the present results show that the common assumption[48,52-56] that the effective polarization potential is zero at $r=0$ cannot be justified in terms of an adiabatic model. The leading long-range nonadiabatic correction to the spherically averaged polarization potential for N_2 at $R=R_e$ has been calculated by Dalgarno *et al.*[46]

Table VI and Fig. 3 show the sensitivity of V^{Pa} to basis set for the approach of the electron along the perpendicular bisector. As for the collinear case, the sensitivity of the adiabatic polarization potential to basis is comparable to the sensitivity of the polarizability and is greater than the sensitivity of the static potential. Thus the smaller basis sets are useful for qualitative predictions but cannot be trusted for quantitative accuracy. It is interesting that the adiabatically polarized potential V^{SPa} is also less sensitive to basis variations than the adiabatic polarization potential, i.e., there is often a cancellation between the change in V^S and the change in V^{Pa} when the basis is changed. However, there are important exceptions, e.g., compare bases 7 and 8 in the range $1.25-2.5a_0$.

It is common to represent semiempirical polarization potentials as

$$V^P(r,\chi)=\sum_{\substack{\lambda=0\\ \lambda\ \mathrm{even}}}^{\lambda^P_{\max}} V^P_\lambda(r)P_\lambda(\cos\chi)\,, \tag{6}$$

where $P_\lambda(\cos\chi)$ is a Legendre polynomial and $\lambda^P_{\max}=2$.[48,52-56] The motivation for this is that $V^P_\lambda(r)$ decreases faster than r^{-4} at large r for $\lambda\neq 0, 2$. If this representation is accepted $V^P_0(r)$ and V^P_2 can be calculated from results at $\chi=0°$ and 90°, and other angles of approach need not be calculated. To test this we performed calculations at two other χ values at $r=2.0a_0$. The results are compared in Table VII to what would be predicted using $\lambda^P_{\max}=2$ and Eq. (6). Thus the assumption of $\lambda^P_{\max}=2$ seems reasonable at least for $r\geq 2a_0$. This means that $V^{SPa}(r,\chi)$ could be calculated reasonably accurately by performing SCF calculations at only two values of χ for each r.

In Table VIII and Fig. 4, we present the $p\sigma$ and $p\pi$ orbital eigenvalues as a function of the position of the negative charge. Table VIII also includes the other orbital eigenvalues. The orbital eigenvalues give a physical picture of a hypothetical collision in which the scattering electron moves infinitesimally slowly. As the electron approaches, the general trend is an increase in the eigenvalues. The ionization potential obtained for the highest occupied molecular orbital using the Koopmans theorem decreases from 16.78 eV with the charge

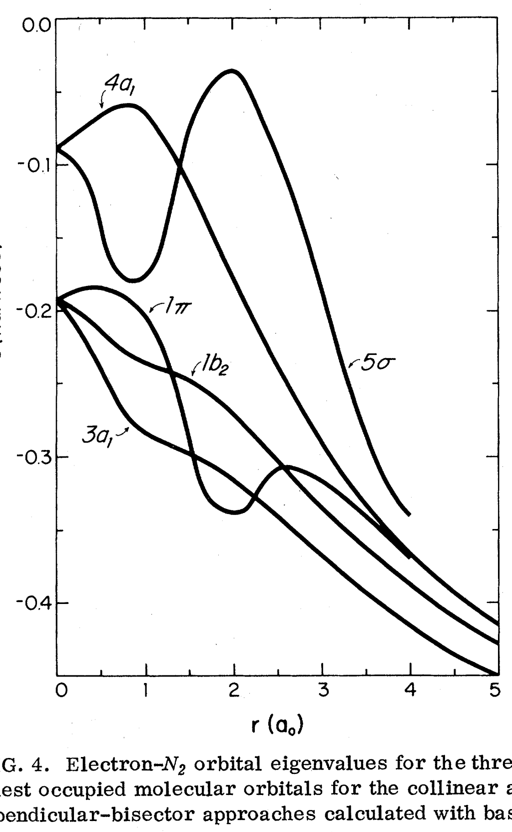

FIG. 4. Electron-N_2 orbital eigenvalues for the three highest occupied molecular orbitals for the collinear and perpendicular-bisector approaches calculated with basis 5. The orbitals are described in Table VIII.

TABLE VIII. Orbital eigenvalues (a.u.) for e^--N_2 with basis 5.[a]

			$\chi = 0°$			
r (a_0)	$\epsilon(1\sigma)$[b]	$\epsilon(2\sigma)$[c]	$\epsilon(3\sigma)$[d]	$\epsilon(4\sigma)$[e]	$\epsilon(5\sigma)$[f]	$\epsilon(1\pi)$[g]
0.50	−15.2768	−14.7042	−0.8573	−0.4133	−0.1427	−0.1842
0.75	−15.2641	−13.4863	−0.9216	−0.3707	−0.1767	−0.1899
1.25	−15.2770	−12.9313	−1.0388	−0.3585	−0.1439	−0.2317
1.50	−15.3509	−14.6158	−1.1491	−0.4191	−0.0771	−0.2868
2.00	−15.4252	−15.4079	−1.2156	−0.4745	−0.0355	−0.3386
2.50	−15.3929	−15.3872	−1.1737	−0.4529	−0.0899	−0.3075
3.00	−15.4088	−15.3545	−1.1788	−0.4675	−0.1821	−0.3167
3.50	−15.4516	−15.3578	−1.2048	−0.4751	−0.2846	−0.3405
4.00	−15.4752	−15.3906	−1.2327	−0.5086	−0.3414	−0.3687
15.00	−15.6246	−15.6168	−1.4131	−0.7100	−0.5662	−0.5450
∞	−15.6896	−15.6860	−1.4800	−0.7773	−0.6338	−0.6168

				$\chi = 90°$			
r (a_0)	$\epsilon(1a_1)$[b]	$\epsilon(1b_1)$[c]	$\epsilon(2a_1)$[d]	$\epsilon(2b_1)$[e]	$\epsilon(3a_1)$[h]	$\epsilon(4a_1)$[h]	$\epsilon(1b_2)$[i]
0.01	−15.2661	−15.2637	−0.8044	−0.4353	−0.1916	−0.0891	−0.1916
0.50	−15.3116	−15.3089	−0.8751	−0.4465	−0.2430	−0.0647	−0.2140
0.75	−15.3359	−15.3329	−0.9320	−0.4494	−0.2694	−0.0594	−0.2277
1.25	−15.3450	−15.3417	−1.0169	−0.4415	−0.2908	−0.0841	−0.2409
1.50	−15.3439	−15.3406	−1.0463	−0.4398	−0.2964	−0.1114	−0.2475
2.00	−15.3567	−15.3533	−1.0982	−0.4521	−0.3154	−0.1787	−0.2716
2.50	−15.3828	−15.3793	−1.1444	−0.4767	−0.3416	−0.2418	−0.3034
3.00	−15.4116	−15.4080	−1.1842	−0.5040	−0.3687	−0.2933	−0.3353
3.50	−15.4386	−15.4350	−1.2174	−0.5299	−0.3935	−0.3344	−0.3639
4.00	−15.4624	−15.4588	−1.2450	−0.5530	−0.4153	−0.3672	−0.3886
5.00	−15.5006	−15.4971	−1.2871	−0.5902	−0.4506	−0.4156	−0.4276
15.00	−15.6232	−15.6196	−1.4135	−0.7110	−0.5676	−0.5501	−0.5505
∞	−15.6896	−15.6860	−1.4800	−0.7773	−0.6338[f]	−0.6168[g]	−0.6168[g]

[a] The general atomic-orbital character of each molecular orbital is given in the footnotes. The e^--N_2 system lies in the xz plane with the molecule on the z axis.

[b] $1s$ bonding.

[c] $1s$ antibonding.

[d] $2s$ bonding.

[e] $2s$ antibonding.

[f] $2p_z$ bonding.

[g] $2p\pi$ bonding.

[h] Linear combination of $2p_x$ and $2p_z$ bonding.

[i] $2p_y$ bonding.

at infinity to 2.43 eV with the charge near the bond midpoint. The highest-occupied-molecular-orbital (HOMO) switches from a $p\pi$ orbital for the charge at infinity to a $p\sigma$ orbital for the charge closer in. A similar physical effect is also seen in the value of the final electronic energy, defined as in Ref. 1, which increases from −132.6674 a.u. with the charge at infinity to −121.495 41 a.u. with the charge $0.01a_0$ from the bond midpoint. These results suggest that the bonding electrons are being destabilized due to the repulsive interaction with the negative charge. However, the total e^--N_2 energy is lower than the value for the electron at infinity due to the attractive interaction of the negative charge with the positive nuclei.

The changes in orbital eigenvalues with r depend strongly on the angle of approach of the charge. This contrasts to the results for H_2 (Ref. 1) where the dependence of the orbital eigenvalue on angle was found to be essentially independent of the angle of approach. Thus, for H_2 we were able to conclude that the interaction of the negative charge with the nuclei provided the dominant portion of the angular dependence of the polarized potential. For N_2 this is clearly not the case. As the electron approaches along the perpendicular bisector, the orbital eigenvalue for the HOMO ($4a_1$) increases until it peaks near $0.75a_0$. The $p\pi$ orbitals split due to the lowering of the symmetry in this approach. For the charge approaching along x, $p\pi_x$, and $p\sigma_z$ orbitals ($3a_1$ and $4a_1$) interact and also split apart with the $p\pi_y$ ($1b_2$) orbital lying between the interacting pair. In the collinear approach, the $p\pi$ do not split and both the $p\sigma$ and $p\pi$ orbital eigenvalues show a complicated dependence on r. The 2σ, 4σ, and 5σ orbitals show a decrease in orbital eigenvalue for the test charge in the region of the nucleus. The 1σ, 3σ, and 1π orbitals also show such a decrease, but at larger r. These decreases presumably correspond to a core polarization effect.

The adiabatic polarization potential computed here cannot be compared directly to experiment. The effective polarization potential for an actual electron-molecule collision contains nonadiabatic effects.[46,48] Since a molecule, however, has less time to respond to a test charge with a nonzero velocity, it is reasonable to assume that the adiabatic polarization model gives an upper limit to the amount of charge polarization. Thus it provides a good starting point for further work.

ACKNOWLEDGMENTS

The authors are grateful to Michael A. Morrison and P. Jeffrey Hay for providing the details of their work (Refs. 11 and 14). This work was supported in part by the National Science Foundation under Grant No. CHE77-27415, by a partial computing time subsidy from the University of Minnesota Computer Center, and by the Alfred P. Sloan Foundation. D.A.D. acknowledges the support of a DuPont Young Faculty Grant (1978).

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