

Electron-molecule scattering theory: An R -matrix study of low-energy elastic e - N_2 collisions in the static-exchange approximation*

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The R -matrix formulation of electron-molecule collision theory is applied to low-energy e - N_2 scattering in the static-exchange approximation. Particular attention is given to the determination of basis sets for such L^2 -variational calculations, and a study of important basis-set characteristics in the context of this collision problem is presented. Results for elastic e - N_2 collisions for scattering energies in the range from about 0.01 to 13.0 eV are reported. The importance of including long-range interactions is briefly discussed.

I. INTRODUCTION

The theoretical analysis of low-energy electron-molecule collisions is complicated by the multi-centered nature of the problem.¹ The lack of spherical symmetry in the electron-molecule interaction potential makes application of standard scattering theory methods such as close coupling² arduous in cases where an exact treatment of effects due to exchange or polarization is required. In response to this predicament, attention has turned in the last few years to a class of approaches which might be called "basis set methods" or, more precisely, " L^2 -variational methods."³ The basic idea underlying these procedures is to make use of the observation that in the region of space near the target molecule, the electron-molecule system resembles in many respects the corresponding negative molecular ion.

This notion has led to a variety of approaches, including the pseudo-bound-state⁴ and related low- l spoiling^{5(a)} approximations, which are appropriate if the effects of partial-wave coupling are short range (e.g., for low-energy s -wave e - H_2 collisions) and, in the case of low- l spoiling, when the effects of the long-range interactions are negligible.^{5(b)} Recently, a more accurate T -matrix expansion technique,⁶ wherein the Lippmann-Schwinger equation for the scattering amplitude is solved in a discrete basis set consisting of Gaussian functions, has been applied to low-energy elastic e - H_2 scattering.⁷ All of these approaches involve the diagonalization of the Hartree-Fock (static-exchange) Hamiltonian in a large basis set made up of L^2 -variational functions.

Another method of this type is based on R -matrix theory. Originally developed by Wigner and Eisenbud⁸ in nuclear physics (see the review by Lane and Thomas⁹) and adapted to a variety of problems in atomic physics by Burke and co-workers,¹⁰ the R -matrix approach was extended to electron-mo-

lecule collision problems by Schneider¹¹ and has been successfully applied to low-energy elastic e - H_2 and e - F_2 scattering.^{12,13}

The selection of basis sets for calculations using any of these methods is critical, as one wishes to use a reasonably small basis set (to make the computations tractable) without ignoring physically important effects. To date, however, no extensive attention has been given to this question. A truly systematic study of basis functions would be prohibitive, since there are a very large number of parameters one could vary in such a study, and of questionable value, since it would likely be highly system dependent. In this paper, we have studied some of the important *characteristic properties* one must incorporate into the basis set for an L^2 -variational calculation to accurately represent the fundamental physics of the collision. In addition, we have determined static-exchange cross sections (converged in basis set) for e - N_2 collisions in the energy range from about 0.01 to 13.0 eV.

The e - N_2 system has become quite important to the developing field of electron-molecule collision theory. In contrast to e - H_2 scattering, this system is sufficiently nonspherical that the full character of the electron-molecule potential is involved. At the same time, it is "small" enough (14 electrons, an internuclear separation of roughly $2a_0$) that highly accurate calculations are feasible. Thus e - N_2 scattering has been the subject of studies using close-coupling,¹⁴ highly approximate Born¹⁵ and distorted-wave,¹⁶ model-exchange,¹⁷ low- l spoiling,⁵ and other methods.¹⁸

In Sec. II of this paper, we briefly recapitulate the conceptual basis of the R -matrix method and present an outline of the procedure used to solve the problem at hand. We also define the theoretical context within which we treat e - N_2 scattering and point out some modifications in the R -matrix procedure as here applied beyond what has previously been reported. In Sec. III we discuss various basis

sets, focusing on general characteristics as they reflect on the physics of the scattering event or on computational facets of the problem. Our final static-exchange results for e - N_2 collisions are presented in Sec. IV together with some remarks on the inclusion of the induced-polarization interaction. We conclude in Sec. V by discussing future directions of this research. Unless otherwise stated, atomic units are used throughout this paper.

II. THEORY AND PROCEDURES

A. Theory

The R -matrix method in *atomic* physics has been recently reviewed by Burke and Robb.¹⁹ The essential idea is the division of configuration space into two regions: an *inner region* "near" the target, where the electron-target interactions are strong, short range, and (in the case of exchange) nonlocal, and an *outer region* "far" from the target, where the interactions are weak, long range, and (usually) known as a simple analytic form (e.g., permanent-quadrupole or induced-polarization terms). A boundary between the two regions, the " R -matrix surface," is defined. The R -matrix at the boundary can be calculated in terms of a set of *discrete* eigenfunctions of the system Hamiltonian which satisfy fixed (but arbitrary) logarithmic boundary conditions on the R -matrix surface. The R matrix, which is a function of the scattering energy, then provides the "connection" between the regions. In the outer region, coupled differential equations are integrated numerically from infinity to the R -matrix surface. The logarithmic derivatives are matched, and the K -matrix, phase shifts, and cross section extracted. In general, then, the most difficult aspects of the problem are incorporated into the discrete eigenfunctions defined in the inner region, which determine the R matrix. These functions can be calculated using standard bound-state procedures and codes. The R matrix thereby obtained is a meromorphic function of energy containing no branch cuts associated with thresholds.

This approach is also desirable because only one diagonalization of the electron-target Hamiltonian is required to study scattering for a wide range of incident energies. Further, resonances are easily located by examination of the poles of the R matrix.

The generalization of this theory to electron-molecule collisions is discussed by Schneider,¹² so we shall only summarize the key points here. The central feature of this application is the expansion of the scattering function in the inner region in a set of *analytic* basis functions, chosen as

floating Gaussians in prolate spheroidal coordinates. Introduction of the Bloch operator²⁰ into the Hartree-Fock equation for the scattering function ensures Hermiticity of the resulting Hamiltonian and allows a simple spectral expansion of the scattering wave function even when the basis functions used satisfy arbitrary logarithmic boundary conditions on the R -matrix surface. A third element of the application of R -matrix theory to electron-molecule scattering is the use of the Buttle correction.²¹ In practice, one has only a finite set of discrete eigenfunctions of the static-exchange Hamiltonian in the internal region with which to calculate the R matrix at the surface. The effect of the neglected levels can be incorporated via the Buttle correction, which requires selection of a zeroth-order Hamiltonian (usually chosen to be the kinetic energy operator) for which the Schrödinger equation can be solved in closed form. The correction is especially useful when for practical reasons one must use a small basis of discrete functions which by themselves inadequately represent the full R matrix. (In the present study, we have chosen to use sufficiently large basis sets that the Buttle correction is not necessary; see Sec. III).

B. Computational procedure

The procedure for carrying out an R -matrix calculation on a problem in electron-molecule scattering has been discussed by Schneider and Hay.¹³ We shall present here only what is required to introduce terminology for our subsequent discussion and to describe the present application. Some procedural differences between the approach used here and that reported in earlier papers in this series will be described.

We have chosen to study low-energy electron collisions with the ground-state ($X^1\Sigma_g^+$) N_2 molecule. The orbital occupancy for this state of the target is

$$X^1\Sigma_g^+ : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 1\pi_u^4.$$

The equilibrium internuclear separation is $R = 2.068a_0$. The nuclei will be held fixed at this separation, and the fixed-nuclei approximation will be made for rotation.²² Therefore the cross sections reported in Sec. IV correspond to averaging over all molecular orientations. The collision will be described in the static-exchange approximation,²³ so that static, exchange, and permanent-quadrupole interactions will be taken into account. (We shall discuss the induced-polarization interaction at the end of this section.) We shall consider Σ_g , Σ_u , Π_g , and Π_u symmetries of the electron-molecule system, where for a $^1\Sigma_g^+$ target state, Σ and Π correspond to the projection of the electron's orbital angular momentum on the axis of quantization (the in-

ternuclear axis $\hat{R}=\hat{z}$). Thus we shall present results for " σ -wave" and " π -wave" scattering. Given this context, the procedure will be described in a series of steps.

(i) We obtain the occupied Hartree-Fock molecular orbitals describing the $X^1\Sigma_g^+$ state of the isolated N_2 molecule. We have used the primitive basis sets of Huzinaga,²⁴ a $9s5p$ basis of nucleus-centered regular Gaussians of the form

$$\varphi_i^j(x, y, z) = x_j^i y_j^m z_j^n e^{-\alpha_i r_j^2} \quad (j=1, 2), \quad (1)$$

where $j=1, 2$ refers to the nuclear centers and i labels each primitive basis function. This set is augmented by $3d$ polarization Gaussians as described by Dunning.²⁵ We use one d -wave polarization function with $\alpha=0.98$. This primitive extended basis set is uncontracted. We have also carried out calculations using the $(9s5p/5s3p)$ contracted basis set of Dunning (see Table II.B of Ref. 26). In any event, the "primitive atomic basis" is used in the program POLYATOM²⁷ to determine the occupied molecular orbitals for N_2 .

The molecular quadrupole moment determined in our fully contracted $(9s5p/5s3p)$ basis is found to be $Q = -1.243ea_0^2$, while in a σ -wave-uncontracted basis (where only atomic orbitals which combine to give molecular orbitals of π symmetry are contracted) we find $Q = -1.249ea_0^2$. These compare adequately with the experimental value²⁸ of $|Q| = 1.04 \pm 0.07ea_0^2$.

(ii) We next augment the primitive atomic basis defined in step (i) with a set of *diffuse* nucleus-centered atomic functions of the form of Eq. (1). The Hartree-Fock (HF) potential energy is then determined on this augmented basis. [One need not use the same primitive atomic basis set in steps (i) and (ii); e.g., it might be desirable to use a contracted basis in step (i) and to uncontract the basis in step (ii). See Sec. III A.]

The diffuse atomic functions are required in order that the augmented basis will be nearly complete over the region of configuration space of interest. In the original R -matrix procedure,¹² the virtual Hartree-Fock orbitals of N_2 would have been determined and used to define the molecular potential energy. However, in the course of this study, we found that linear dependence of the molecular orbitals poses considerable problems, particularly in the π -wave scattering calculations. To avoid this difficulty, we now simply diagonalize the overlap matrix in the augmented atomic basis and delete linearly dependent functions from the resulting set of eigenvectors. This new procedure obviates the necessity for calculating molecular virtual orbitals and resolves the linear-dependence problem mentioned above. The diffuse functions must be chosen with care lest the basis set repre-

sentations of the kinetic energy and potential energy operators be inequivalent. We shall define the augmented basis further and discuss selection of the diffuse functions in Sec. III.

(iii) The Hartree-Fock potential energy, which was calculated in step (ii) on the augmented atomic basis, is now transformed to the orthonormal molecular basis consisting of the bound molecular orbitals plus the eigenvectors of the overlap matrix.

(iv) We now turn to the scattering function and select an R -matrix basis of free functions. These are chosen to be elliptic floating Gaussians of the form

$$\chi_i(\xi, \eta, \phi) = \xi^{\beta_i} \eta^{\alpha_i} [(\xi^2 - 1)(1 - \eta^2)]^{\nu_i/2} \times e^{-\beta_i \eta} e^{-\alpha_i (\xi - A_i)^2} \begin{Bmatrix} \sin \nu_i \phi \\ \cos \nu_i \phi \end{Bmatrix}, \quad (2)$$

where $\nu_i=0$ (1) for σ (π) symmetry. The center of the function χ_i is A_i , and α_i and β_i are parameters.

The basis set chosen for this calculation can be found in Table II of Ref. 13. We transform the molecular HF potential calculated in step (iii) to the R -matrix basis of free functions using the insertion technique of Schneider¹¹ and diagonalize the static-exchange Hamiltonian for the scattering electron,

$$\mathcal{H} = -\frac{\nabla^2}{2} - Z \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} \right) + \sum_{i=1}^n (2J_i - K_i), \quad (3)$$

where Z is the nuclear charge, n is the number of molecular orbitals ($n=7$ for N_2) and J_i and K_i are the usual Coulomb and exchange operators.²⁹ The resulting eigenfunctions are used to calculate the R matrix. It is important to stress that the calculations in steps (i)–(iv), while time consuming, need only be carried out once since they are independent of the scattering energy.

(v) In the final step, we solve the differential scattering equations¹² in the outer region, integrating (via the Numerov algorithm³⁰) from infinity to the R -matrix surface,³¹ and determine the K matrix. For this calculation, the surface was chosen at $\xi = 7a_0$, which corresponds to $r \approx 10a_0$. For the e - N_2 system, this value of ξ is large enough that the exchange and short-range electrostatic interactions are negligible beyond the R -matrix surface, leaving only the simple analytic long-range terms in the potential energy. From the K matrix, differential and total cross sections can easily be calculated.³²

The long-range interactions which are most important in the energy range under consideration are the permanent-quadrupole and induced-polarization terms. In spherical coordinates, the form of the

long-range potential energy is

$$V_{\text{LR}}(\vec{r}) \underset{r \rightarrow \infty}{\sim} \frac{\alpha_0}{2r^4} - \left(\frac{\alpha_2}{2r^4} + \frac{Q}{r^3} \right) P_2(\cos\theta), \quad (4)$$

where α_0 and α_2 are the spherical and nonspherical polarizabilities³³ of N_2 , $\alpha_0 = 11.89a_0^3$, $\alpha_2 = 4.19a_0^3$, and Q is the permanent quadrupole moment (see step (i) above]. In prolate spheroidal coordinates, taking into account the fact that we are far from the target, Eq. (4) becomes

$$V_{\text{LR}}(\xi, \eta) = -\frac{8\alpha_0}{\xi^4 R^4} - \left(\frac{8\alpha_2}{\xi^4 R^4} + \frac{8Q}{\xi^3 R^3} \right) P_2(\eta). \quad (5)$$

In the static-exchange calculations reported in Sec. IV, the R -matrix surface is chosen at a radial distance of $10a_0$ from the center of mass of the N_2 target. Beyond this radius, the low-order partial waves that contribute to the cross section are effectively uncoupled for low scattering energies.^{5(a)} Therefore, for $r > 10a_0$, we have included only the diagonal quadrupole matrix elements $\langle lm|P_2|lm\rangle$. That is, we solve *uncoupled* differential equations in the external region. Five partial waves (s, p, d, f, g) are taken into account in this region. We shall discuss the effects of including the induced-polarization terms in Sec. IV.

III. CHOICE OF BASIS SETS

As in any variational procedure (e.g., calculation of bound-state wave functions for atomic or molecular systems), the key to successful application of the R -matrix method to problems in electron-molecule collision theory is the choice of basis sets. We have introduced three basis sets in Sec. II: (1) the *primitive atomic basis* of step (i), which describes the occupied target molecular orbitals; (2) the *augmented atomic basis* of step (ii), which includes the primitive atomic basis functions plus diffuse functions required for the transformation of the HF potential via the insertion technique; and (3) the *analytic R -matrix basis* of free elliptic floating Gaussians. In general, the idea is to pick a primitive atomic basis which accurately represents the core (occupied) molecular orbitals. The use of contracted functions is appealing in HF calculations because it can reduce the size of the basis.³⁴ In the choice of the diffuse basis, one must select functions which overlap sufficiently with the analytic R -matrix functions to satisfy closure in the transformation of the molecular HF potential [see Eq. (11) of Ref. 12 and accompanying discussion]. Finally, the analytic R -matrix basis must be sufficiently flexible to accurately represent the scattering function in the inner region.

In this section, we shall discuss three points beyond these rather obvious remarks: (1) the effects

TABLE I. Description of the augmented atomic basis sets used in this study of elastic e - N_2 collisions. The analytic R -matrix basis can be found in Table II of Ref. 13. The various columns are described in Sec. III of the text. In the column labeled "Diffuse functions," r is the geometric ratio used.

Basis set	Symmetry	Contraction	Diffuse functions	No. of at. orbs.
1	σ	σ cont.	s, p_z	86
2	σ	σ uncontracted	s, p_z	98
3	π	π cont.	p_y ($r = 1.7$)	62
4	π	π uncontracted	p_y ($r = 1.7$)	70
5	π	π uncontracted	p_y ($r = 1.4$)	82
6	π	π uncontracted	p_y ($r = 1.4$), d_{yz} ($r = 1.7$)	98
7	π	π uncontracted	p_y ($r = 1.7$), 10 tight p_y	80

of contraction in the primitive atomic basis; (2) the selection of diffuse functions for the augmented atomic basis; and (3) the importance of including free functions which are primarily localized in the target region in the analytic R -matrix basis. To study these and other aspects of basis-set selection, we have carried out full static-exchange e - N_2 calculations using *seven* different augmented atomic basis sets. In order to avoid an extensive list of functions, we have made the tabulation of these basis functions available on request from the authors in a separate document.³⁵ The salient features of each basis set are summarized in Table I.

Briefly, sets 1 and 2 are used for σ -wave scattering calculations while 3–7 are for π -wave calculations. In sets 1 through 4 we change the primitive atomic basis used to represent the occupied molecular orbitals, while in 5–7 we alter the character of the diffuse functions. The analytic R -matrix basis is the same for all seven cases (see Ref. 13). Additional calculations in which certain types of free functions in this basis are removed will be discussed in Sec. III C.

In all σ -wave (π -wave) calculations, the primitive s and p atomic functions contributing to the π (σ) occupied molecular orbitals are contracted. In basis 1 (3) the σ (π) symmetry s and p atomic orbitals are also contracted, while in basis 2 (4) they are uncontracted. The d -wave polarization functions are not contracted in any case.

The exponents α_i in Eq. (1) for all the diffuse atomic orbitals are chosen by a geometric progression. Tabulations of these bases can be found in Ref. 35. In sets 4 and 7, only diffuse nucleus-centered p_y Gaussians were included with a geo-

TABLE II. Eigenvalues of the static-exchange Hamiltonian for e - N_2 scattering for the bound molecular orbitals in atomic units. Table IIA contains the σ orbitals and Table IIB the π orbitals. Primed basis sets do not contain tight free functions in the analytic R -matrix basis (see Sec. IIIC). The column labeled SCF contains the molecular-orbital energies determined from a HF calculation on $N_2(X^1\Sigma_g^+)$ as described in the text.

IIA					
	1	1'	2	2'	SCF
$1\sigma_g$	-16.2188	-15.7092	-15.6808	-15.6805	-15.6785
$2\sigma_g$	-1.5546	-1.4847	-1.4767	-1.4764	-1.4758
$3\sigma_g$	-0.7721	-0.6882	-0.6332	-0.6326	-0.6310
$1\sigma_u$	-16.1810	-15.7080	-15.6771	-15.6769	-15.6749
$2\sigma_u$	-0.8523	-0.8140	-0.7754	-0.7752	-0.7747
IIB					
	3	3'	4	4'	SCF
$1\pi_u$	-0.7429	-0.6716	-0.6173	-0.6167	-0.6130

metric ratio of 1.7 (the smallest exponent α_i being 3×10^{-4}). In sets 5 and 6, a larger set of p_y functions was used, with a geometric ratio of 1.4 (the smallest $\alpha_i = 1 \times 10^{-4}$). In addition, diffuse d_{yz} Gaussians were included in set 6 (ratio = 1.7, smallest $\alpha_i = 2.9 \times 10^{-3}$). The addition of diffuse d_{yz} functions in the case of π -wave scattering is partly suggested by our desire to accurately represent the Π_g d -wave resonance in e - N_2 scattering. Finally, in basis 7 we supplemented the diffuse p_y functions of basis 4 with ten *additional* p_y functions localized in the region of the target. These were interspersed among the core functions. Introduction of these additional functions was an attempt to improve the completeness of the augmented atomic basis. In the present discussion, we wish to emphasize the changes in the results obtained as we alter the nature of the basis; our final e - N_2 results will be presented in Sec. IV. (In all cases below, only illustrative results will be shown. More complete tabulations are available in Ref. 35.)

A. Contraction in the primitive atomic basis

In a prior study of e - F_2 scattering, it was found¹³ to be important to ensure that the primitive atomic basis not be overcontracted. In particular, a completely contracted basis provides an insufficient number of molecular functions to transform the HF potential to the R -matrix basis. The effects of contraction on the scattering are reflected in the eigenvalues of the static-exchange Hamiltonian [Eq. (3)], which can be determined by a diagonalization in the full R -matrix basis. Since the basis includes the occupied molecular orbitals (MO) along with the analytic free functions, this calculation should reproduce the bound eigenvalues. In Table II we compare these eigenvalues for the occupied

σ and π orbitals against the self-consistent-field (SCF) results obtained from a HF-SCF-MO calculation on the N_2 target using the uncontracted ($9s5p1d$) basis defined in Sec. II. Notice that the least-tightly-bound orbitals are the most poorly represented. The effect of contraction on the eigenphases³⁶ is shown in Table III for a few selected energies for s_σ , p_σ , p_π , and d_π scattering. The effects of contraction of the primitive atomic basis are seen to be the greatest in the case of π -wave scattering, although some improvement in both σ - and π -wave results is obtained when the basis is uncontracted.

The dramatic effect of contraction in the π -wave

TABLE III. Eigenphases for σ -wave (III A) and π -wave (III B) static-exchange e - N_2 scattering in various basis sets which differ in their treatment of the primitive atomic basis set (see Sec. IIIA).

III A					
k (a.u.)	E (eV)	s_σ -wave		p_σ -wave	
		1	2	1	2
0.017	0.004	-0.036	-0.036	0.0	0.0
0.066	0.059	-0.142	-0.142	0.0	-0.002
0.135	0.248	-0.289	-0.290	-0.001	-0.012
0.222	0.670	-0.471	-0.477	-0.011	-0.049
0.577	4.527	-1.209	-1.275	-0.386	-0.488
III B					
k (a.u.)	E (eV)	p_π -wave		d_π -wave	
		3	4	3	4
0.072	0.070	0.001	-0.001	0.0	0.0
0.114	0.177	0.005	-0.004	-0.002	0.0
0.187	0.475	0.017	-0.016	-0.018	0.001
0.393	1.481	-0.033	-0.131	-0.190	0.095
0.894	10.866	-0.586	-0.709	-0.355	2.501

case is further illustrated by the fact that the diagonalization of the static-exchange Hamiltonian for basis 3 reveals the presence of an unphysical bound state (with an energy of -0.038 a.u.). Note from Table II that the $1\pi_u$ molecular orbital is bound by about 0.1 hartree more than is the SCF result. Finally, the well-known $e-N_2 \Pi_g$ shape resonance^{37,38} at about 2.3 eV does not appear at all in this energy range if the basis of π -wave functions is contracted.

These results suggest the need for sufficient flexibility in those basis functions which are concentrated in the core (target) region to ensure substantial overlap with both the occupied molecular orbitals and the analytic free functions. If too many of the virtual orbitals are removed by contracting the primitive atomic functions, a poor representation of the HF potential for the scattering problem may result. This problem can be overcome by uncontracting the basis (which can be very expensive for the SCF calculation) or by putting the HF potential on a large basis *after* carrying out the SCF-MO calculation of the bound-target orbitals. The latter procedure requires handling many more integrals and increases the time required for the transformation [step (iii) of Sec. II] but is nonetheless preferable to using a completely uncontracted basis at the SCF stage of the calculation.

B. Diffuse functions

The relative insensitivity of our σ -wave phase shifts seen in Table II suggests that our σ -wave basis 2 is quite good. The construction of a basis

TABLE IV. Eigenphases for π -wave static-exchange $e-N_2$ scattering in various basis sets which differ in the diffuse atomic functions used in the augmented atomic basis (see Sec. III B).

k (a.u.)	E (eV)	IV A		
		p_π -wave	5	6
0.172	0.402	-0.013	-0.013	-0.014
0.553	7.519	-0.314	-0.322	-0.308
0.830	9.366	-0.649	-0.669	-0.653
k (a.u.)	E (eV)	IV B		
		d_π -wave	5	6
0.273	1.013	0.009	0.010	0.010
0.393	2.100	0.082	0.084	0.084
0.518	3.648	0.904	0.899	0.892
0.631	5.413	2.364	2.397	2.403
0.894	10.866	2.500	2.511	2.510
1.182	18.995	2.401	2.402	2.402

TABLE V. Comparison of R -matrix static-exchange eigenphases for $e-N_2$ scattering with the low- l spoiling results of Ref. 5(a). Basis 2' was used for the s_σ and p_σ calculations and basis 6 for the p_π and d_π cases (see Table I). In these calculations no long-range interactions are included beyond $\xi = 7a_0$, the R -matrix boundary.

Symmetry	k (a.u.)	Low- l spoiling	R matrix
s_σ	0.017	-0.041	-0.037
	0.066	-0.16	-0.144
	0.179	-0.42	-0.388
	0.491	-1.05	-1.08
p_σ	0.135	-0.015	-0.012
	0.361	-0.19	-0.176
	0.577	-0.48	-0.489
	1.098	-1.4	-1.28
p_π	0.114	-0.006	-0.004
	0.253	-0.052	-0.039
	0.372	-0.132	-0.116
	0.830	-0.592	-0.669
d_π	0.393	0.06	0.084
	0.518	0.09	0.899
	0.631	2.35	2.397
	0.894	2.52	2.511
	1.182	2.33	2.402

for the π -wave symmetries has been studied beyond the question of contraction. In particular, we have examined the choice of the diffuse functions which, together with the primitive atomic Gaussians, make up the augmented atomic basis. In the case of π -wave scattering, we focused our attention on the representation of the Π_g d -wave resonance. Three basis sets, 5, 6, and 7 in Table I, were considered. Results for p_π - and d_π -wave scattering in these basis sets are shown in Table IV. Not surprisingly, the best results are achieved with the largest basis, 6, which includes both p_y and d_{yz} nucleus-centered Gaussians. Including the latter functions does significantly alter the eigenphases, bring the p_π -wave results into better agreement with other published results (see Table V). The addition of diffuse functions in the core region (cf. basis 7) appears not to substantially improve our results. In all cases, the Π_g resonance is present, although at too high an energy.

C. The analytic R -matrix basis

The basis of free elliptic floating Gaussians [see Eq. (2)] used in the above calculations¹³ consists of 94 functions. Some of these are centered at the center of mass of the molecule and have fairly large exponents α_i and β_i ; i.e., they are concen-

trated in the region of the target molecule. The use of these functions with a contracted basis of primitive atomic functions can lead to inconsistencies in the calculation. We have found that deleting the tight origin-centered free functions³⁵ from the analytic R -matrix basis usually improves the results. As Table II illustrates, the new basis sets, denoted 1' and 2' for σ -wave scattering and 3' and 4' for the π -wave case, yield eigenvalues for the occupied orbitals in better agreement with the SCF results than those obtained with the unprimed bases. The phase shifts are also improved somewhat, as can be seen by comparing the columns labeled "2" in Table III with those labeled "2'" in Table V.

In the π -wave scattering calculations, we must distinguish the nonresonant (p_π) symmetry from the resonant (d_π) symmetry. In the former case, the change produced by deletion of the "tight" free functions is not pronounced. In the d_π resonant symmetry, deletion of these functions causes the shape resonance to vanish in all basis sets studied (3-7). This observation is consistent with the fact that the amplitude of the resonant wave function is largely confined to the region of the target molecule. In order to study this result further, we decomposed each of the eigenvectors of the static-exchange Hamiltonian by expanding in an orthonormal set consisting of the eigenvectors of the overlap matrix. We find that the resonance pole of the R matrix at 0.199 hartrees (~ 5.4 eV) vanishes when the tight origin-centered functions are removed from the analytic R -matrix basis. In fact, about 90% of the particular eigenvector which corresponds to this pole arises from these functions. (It is interesting to note that none of these important tight functions has significant d -wave character at the R matrix surface.) Thus inclusion of these functions, while undesirable in general, is essential to treat scattering in a symmetry where a shape resonance is present.

IV. RESULTS FOR e -N₂ SCATTERING

In the above section, we have discussed some of the properties which should characterize the various basis sets required in our L^2 -variational calculation of electron-molecule scattering. Based on this study, we selected as optimum basis sets for the e -N₂ calculations basis 2' for σ -wave and basis 6 for π -wave scattering (see Table I). Both sets have uncontracted primitive basis sets (for σ and π functions, respectively). Basis 2' has no "tight" free functions, but basis 6 does contain these functions, since the resonance appears in the Π_g symmetry.

This choice of basis sets was based in part on

TABLE VI. Eigenphases for e -N₂ scattering in s_σ , p_σ , p_π , and d_π symmetries at selected energies. The "no LR" numbers set the long-range interaction potential to zero beyond $\xi = 7a_0$. The "Quad." numbers contain the permanent quadrupole interaction in the outer region, and the "Pol." numbers include quadrupole and induced dipole interactions in the outer region.

k (a.u.)	Symmetry	No LR	Quad.	Pol.
0.1	s_σ	-0.217	-0.217	-0.167
	p_σ	-0.005	-0.027	-0.009
	p_π	-0.003	-0.008	-0.023
	d_π	0.0	-0.002	0.001
0.3	s_σ	-0.650	-0.650	-0.627
	p_σ	-0.111	-0.135	-0.102
	p_π	-0.064	-0.051	-0.024
	d_π	-0.017	-0.010	0.032
0.5	s_σ	-1.103	-1.103	-1.097
	p_σ	-0.368	-0.377	-0.366
	p_π	-0.253	-0.249	-0.241
	d_π	-0.603	-0.599	-0.611
1.0	s_σ	-1.281	-1.281	-1.286
	p_σ	-1.134	-1.139	-1.132
	p_π	-0.810	-0.807	-0.803
	d_π	-0.670	-0.672	-0.666

physical arguments concerning the need for an adequate representation of the HF potential and of the scattering function as suggested in Sec. III and partly by a study of the bound eigenvalues of the static-exchange Hamiltonian (see Table II).

Of the published theoretical studies of low-energy e -N₂ scattering, the one which most closely resembles ours in its treatment of the physics of the collision is the low- l spoiling calculation of McKoy *et al.*^{5(a)} In Table V, we compare our R -matrix static-exchange eigenphases for s_σ , p_σ , p_π , and d_π scattering with the low- l spoiling results from Ref. 5(a) at selected energies. In these calculations we have set $Q = 0$ in the outer region to facilitate this comparison. Of course, the full quadrupole interaction is included in the potential energy inside the R -matrix surface.

The effect on the eigenphases of including the long-range diagonal quadrupole interaction term for $r > 10a_0$ can be seen in Table VI. As expected, the effect of this interaction on the eigenphase shifts is greatest at the lower incident energies. However, at very low energies ($k^2 \leq 0.01$ Ry), e -N₂ scattering is essentially pure s wave,¹⁷ i.e., the total cross section is determined from the s_σ eigenphase shift, and the effect of the quadrupole interaction is somewhat mitigated.

The final static-exchange e -N₂ eigenphases for s_σ , p_σ , p_π , and d_π scattering are plotted in Fig. 1. The corresponding total cross sections are shown

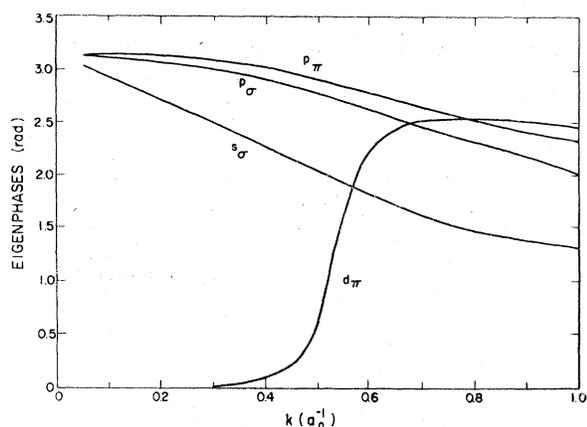


FIG. 1. Static-exchange eigenphases (in rad) for e - N_2 scattering for s_σ , p_σ , p_π , and d_π symmetries. Bases 2' and 6 were used for σ and π symmetries, respectively. The long-range diagonal quadrupole interaction was included in the solution of the coupled equations for $\xi > 7.0a_0$ with $Q = -1.249ea_0^2$.

in Fig. 2 and representative differential cross sections in Fig. 3. The Π_g resonance occurs at ~ 5.4 eV in these static-exchange calculations.

These results do not take into account the effects of induced polarization. These are known to be important in low-energy electron-molecule scattering.³⁹ For example, in e - H_2 collisions the qualitative behavior of the cross sections below a scattering energy of about 0.25 eV is determined by the

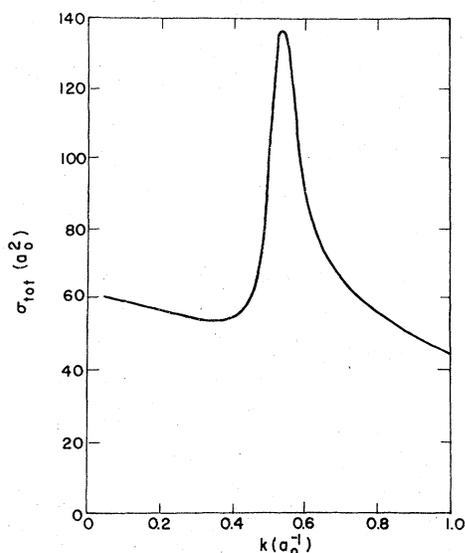


FIG. 2. Total (integrated) static-exchange cross sections (in a_0^2) for e - N_2 collisions including s_σ , p_σ , p_π , and d_π symmetries and the long-range diagonal quadrupole interaction with $Q = -1.249ea_0^2$.

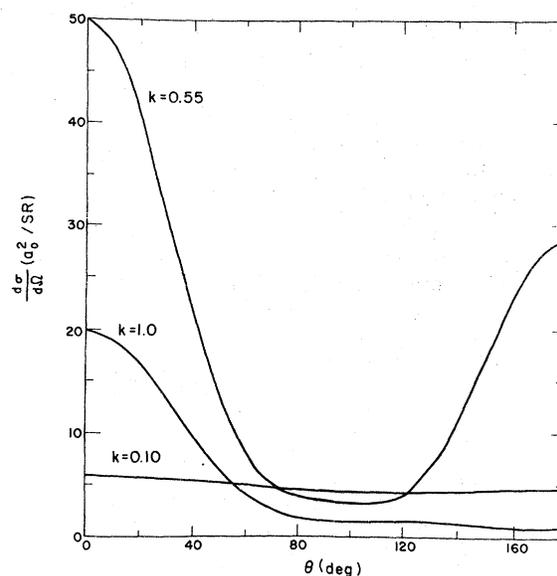


FIG. 3. Differential cross sections for e - N_2 scattering in the static-exchange approximation including s_σ , p_σ , and d_σ symmetries. Three energies are shown: $k = 0.10a_0^{-1}$ ($E = 0.14$ eV), $k = 0.55a_0^{-1}$ ($E = 4.11$ eV), and $k = 1.0a_0^{-1}$ ($E = 13.60$ eV). The long-range diagonal quadrupole interaction is included with $Q = 1.249ea_0^2$.

presence or absence of the induced-polarization interaction in the theoretical formulation of the problem.

In Table VI we show the effect on the eigenphases of including the *diagonal* matrix elements due to the polarization interaction in the outer region (i.e., for $\xi \geq 7a_0$). However, this modification is not sufficient to fully correct for neglect of polarization, since this interaction is effective for $\xi < 7a_0$. A number of theories of electron-molecule scattering incorporate polarization effects semi-empirically, using a cutoff function to truncate the polarization term in the potential energy, Eq. (4), at some cutoff radius.^{14,18,39} An alternate procedure is to introduce pseudostates into the representation of the system wave function in the inner region.⁴⁰ Pseudostates are essentially distorted electronic states which represent the effects of the polarization interaction. We are at present pursuing such a calculation for e - N_2 scattering.

V. CONCLUSIONS

In this paper, we have reported an *ab initio* static-exchange calculation of low-energy e - N_2 scattering. Within the framework provided by this problem, we have studied the question of basis-set selection hoping to provide guidance for future L^2 -variational calculations. We have found that, in general, uncontracted basis sets are necessary to

provide accurate L^2 representations of the HF potential. Moreover, care must be exercised in selection of basis functions to represent the scattering function in cases where a shape resonance is present in the electron-molecule symmetry under consideration.

With this study, we feel that the treatment of low-energy electron scattering from closed-shell targets in the static-exchange approximation by the R -matrix method is well in hand. We must now turn to an accurate treatment of the polarization interaction (as discussed in Sec. IV) to complete

the analysis of elastic scattering.

Beyond this, work is underway on the R -matrix treatment of electronic excitation in diatomic molecules by electron impact, with initial attention focused on e - H_2 collisions.⁴¹

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