

Electron scattering by diatomic molecules: Iterative static-exchange techniques

L. A. Collins and W. D. Robb

Theoretical Division, Group T-4, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

M. A. Morrison

Department of Physics and Astronomy, University of Oklahoma, Norman, Oklahoma 73019

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Iterative techniques are developed and examined for the solution of the single-center, fixed-nuclei electron-molecule scattering equations. They are found to have wide application to scattering by both large and small homo- and heteronuclear diatomic molecules. It is found that enforcement of orthogonality of the bound and continuum orbitals is required for efficient convergence with iteration. Results are presented for the molecules H_2 , N_2 , LiH , and CO .

I. INTRODUCTION

Recent developments in close-coupling and L^2 methods have made possible the exact treatment of exchange in low-energy electron-molecule collisions. Although most calculations have been confined to the static-exchange (SE) approximation, results for electronic excitations, both direct¹ and virtual,² have been reported. L^2 approaches have centered on the R -matrix³ and T -matrix⁴ techniques, while the major close-coupling approaches have included noniterative integral⁵ and differential^{6,7} equations, algebraic equations,⁸ and iterative integral equations⁹ methods. Each approach manifests certain advantages: the L^2 methods in their direct account of the multicenter nature of the molecular potential and the close-coupling techniques in their highly systematic convergence.

Within the close-coupling formulation, the major distinction rests between iterative and noniterative techniques. In the noniterative approach an additional coupled equation arises from each unique exchange kernel. Therefore the number of coupled equations is always larger than that for the static solution. Since the solution of the coupled equations involves matrix operations whose execution time scales as the cube of the number of equations, the noniterative approach can lead to greatly increased computation times over the static case. On the other hand, in the iterative approach the number of coupled equations never exceeds that of the static solution. The computation time is proportional to the time needed to calculate the static solution and evaluate the exchange integrals multiplied by the number of iterations. A drawback to this approach lies in the possibility that the iterative series can diverge.

In an earlier Letter^{9(a)} we reported preliminary results for SE electron-molecule collisions calculated with an iterative close-coupling method. In applying the iterative method to e -molecule collisions, we have modified several of the more successful techniques for treating e -atom collisions.^{9(b)} The electron-molecule collision problem was formulated in the body frame making the fixed-nuclei approximation,¹⁰ and the bound and continuum orbitals were expanded in spherical harmonics about the center of mass of the molecule. The close-coupling approximation was invoked, by which the single-center expansions were truncated at finite l values. We solved the resulting set of coupled integro-differential equations iteratively using an integral equations algorithm. In Sec. II we present a more detailed formulation of the iterative method. The basic form of the SE equations is taken from an earlier paper by Morrison and Collins¹¹ (hereafter referred to as I). The reader is referred to this paper for a more extensive derivation. We follow this discussion in Sec. III with a presentation of our results for e - H_2 , $-N_2$, $-LiH$, and $-CO$ collisions. Section IV is reserved for a summary of our findings.

II. THEORY

A. Scattering equations

In the body-frame fixed-nuclei approximation the SE equations [from I, Eq. (2.15)] are

$$\begin{aligned} & \left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + k^2 \right) F_{i_i j}^{(m)}(r) \\ &= 2 \sum_{i_k} \left(V_{i_i i_k}^{(m)}(r) F_{i_k i_j}^{(m)}(r) \right. \\ & \quad \left. - \int K_{i_i i_k}^{(m)}(r, r') F_{i_k i_j}^{(m)}(r') dr' \right), \end{aligned} \quad (1)$$

where $V_{i_i k}^{(m)}(r)$ is the static potential [I, (2.16)–(2.18)], $K_{i_i k}^{(m)}(r, r')$ is the exchange kernel [I, (2.21)] $F_{i_i k}^{(m)}(r)$ is the radial continuum wave function labeled by the angular momentum l_i of the incident electron and the particular independent solution l_j [the $f_{i_i 0}^{(m)}$ of I, (2.15)], and h^2 is the energy of the incident electron in rydbergs. We have made the close-coupling approximation¹² in which the infinite expansions of the bound and continuum orbitals have been truncated at a finite number of channels. We can thus write Eq. (1) in a compact matrix notation as

$$\underline{\Delta} \underline{F} = \underline{V} \underline{F} + \underline{W}(\underline{\phi}_i, \underline{F}; r) \quad (2)$$

or

$$(\underline{\Delta} - \underline{V}) \underline{F} = \underline{W}, \quad (3)$$

where $\underline{\Delta}$ is the energy-dependent, diagonal differential operator of the left-hand side of Eq. (1), \underline{V} is the static potential, and \underline{W} is the exchange term which involves the integral over the kernel and continuum wave function. We use $\underline{\phi}_i$ to represent the i th occupied orbital of a target molecule with N_{oc} such orbitals [I, (2.7)]. The term $\underline{\phi}_i$ is a column vector whose components are the radial expansion coefficients of the orbital [i.e., the $u_{\mu}^{(m_i)}(r)$ of I, (2.20)].

B. Iterative procedure

To solve Eq. (3) iteratively, one starts with the static (S) solution \underline{F}^0 which solves

$$(\underline{\Delta} - \underline{V}) \underline{F}^0 = 0 \quad (4)$$

and uses it to obtain a zeroth approximation to the exchange potential $\underline{W}^0 = \underline{W}(\underline{\phi}_i, \underline{F}^0; r)$. One then solves successively the set of equations

$$\begin{aligned} (\underline{\Delta} - \underline{V}) \underline{F}^0 &= 0, \quad (\underline{\Delta} - \underline{V}) \underline{F}^1 = \underline{W}^0, \dots, \\ (\underline{\Delta} - \underline{V}) \underline{F}^n &= \underline{W}^{n-1}, \end{aligned} \quad (5)$$

until convergence in the function \underline{F} is attained (i.e., $\underline{F}^{n-1} = \underline{F}^n$).

We employ two methods for solving Eq. (5):

1. Wave-function inverse (WFI) method

We use the fact that in the limit of convergence in Eq. (5)

$$(\underline{F}^{n-1})^{-1} \underline{F}^n = \underline{1}. \quad (6)$$

We then convert the inhomogeneous Eq. (5) to a homogeneous equation of the form

$$(\underline{\Delta} - \underline{V} - \underline{V}_{ex}^{n-1}) \underline{F}^n = 0, \quad (7)$$

where

$$\underline{V}_{ex}^{n-1} \equiv \underline{W}^{n-1} \cdot (\underline{F}^{n-1})^{-1}.$$

This procedure is similar in form to one applied

by Tully and Berry.¹³ The function \underline{V}_{ex}^{n-1} has singularities at the nodes of \underline{F}^{n-1} . However, in the integral equations formulation, we must calculate integrals involving the quantities $\underline{V}_{ex}^{n-1} \underline{F}^n$ rather than \underline{V}_{ex}^{n-1} . The function $\underline{V}_{ex}^{n-1} \underline{F}^n$ is smooth, since the nodes of \underline{F}^{n-1} and \underline{F}^n are usually quite close.

In the case of target molecules which produce reasonably strong coupling potentials, it is necessary to maintain linear independence of the columns of the solution matrix \underline{F} during its outward propagation.¹⁴ This is accomplished by transforming \underline{F} to upper triangular form $\underline{\bar{F}}$ at a given radial distance through a transformation matrix \underline{c} such that

$$\underline{\bar{F}}^n = \underline{F}^n \underline{c}^n. \quad (8)$$

We then propagate $\underline{\bar{F}}^n$ until another transformation is needed. The procedure is repeated until the asymptotic matching radius is reached.

2. Inhomogeneous (I) method

In this method we solve the equation

$$(\underline{\Delta} - \underline{V}) \underline{F}^n = \underline{W}^{n-1}. \quad (9)$$

The most general solution $\underline{\bar{F}}^n$ of Eq. (9) contains an arbitrary amount of the homogeneous (static) solution \underline{F}^0 , and we use this property to retain linear independence of the solutions by choosing \underline{c} in the equation

$$\underline{\bar{F}}^n = \underline{F}^n + \underline{F}^0 \underline{c}^n \quad (10)$$

at specific points during outward integration, so that $\underline{\bar{F}}^n$ is a unit matrix. It is important to note the difference between stabilization procedures given by Eqs. (8) and (10) for homogeneous and inhomogeneous equations, respectively.

C. Orthogonality equations

An important implicit assumption in the derivation of Eq. (1) is that the Pauli principle has excluded the incident electron from occupying any of the bound target orbitals. Such is the case for closed-shell molecules, and the principle applies through the orthogonality condition

$$\int_0^\infty \phi^i F dr = 0 \quad (11)$$

for all bound orbitals $\phi^i(r)$ of the same symmetry as \underline{F} .

These orthogonality conditions, if applied simultaneously with the solution of Eqs. (7) and (9), correctly constrain the nodal structure of the solutions \underline{F} and hence greatly accelerate the convergence of Eq. (5).

We may view this procedure as yielding a much better initial guess for the wave function (since

the initial orthogonalization produces an approximately correct nodal structure) and as confining subsequent iterations to the correct number of nodes. For low-energy collisions (< 2 Ry) we find that the static solution is a good initial guess for the wave function for symmetries without corresponding bound orbitals. We impose the orthogonality constraints, using the technique of Burke and Chandra,¹⁵ by modifying Eq. (3) to

$$(\underline{\Delta} - \underline{V})\underline{F}' = \underline{W} + \sum_i \underline{\phi}^i \underline{\lambda}^i, \quad (12)$$

where

$$\underline{F}' = \underline{F} + \sum_i \underline{P}^i \cdot \underline{\lambda}^i \quad (13)$$

and the $\underline{\lambda}^i$ are Lagrange multipliers determined through the condition (11). The \underline{P}^i terms are column vectors whose components are radial expansion coefficients which solve Eqs. (14) or (15) and are labeled by the orbital angular momentum of the incident electron. The Lagrange multipliers are row vectors whose components are labeled by a particular linearly independent solution. Thus $\underline{P}^i \cdot \underline{\lambda}^i$ is a matrix with rows and columns labeled as those of \underline{F} .

The solutions \underline{P}^i are determined differently for the two methods mentioned above. For the WFI method,

$$(\underline{\Delta} - \underline{V} - \underline{V}_{\text{ex}}^{n-1})\underline{P}^i = \underline{\phi}^i, \quad (14)$$

with \underline{F}' used to calculate $\underline{V}_{\text{ex}}$, and for the inhomogeneous method,

$$(\underline{\Delta} - \underline{V})\underline{P}^i = \underline{\phi}^i. \quad (15)$$

Since Eqs. (14) and (15) are inhomogeneous, the solution cannot be made linearly independent during outward propagation by the transformation in Eq. (8). Such a constant transformation would scale the right-hand side of the equation, with the result that the transformed \underline{P}^i would no longer satisfy the original equations. We therefore must guarantee linear independence of the \underline{P}^i solutions by the procedure given in Eq. (10).

Where orthogonality is included in the methods, we will refer to them by the abbreviations OWFI and OI.

D. Inherent problems with iterative schemes

1. OWFI method

The main problem with this method is that the orthogonalized solutions $\underline{F}'(r)$ of Eq. (13) are dominated at small r values by the terms $\underline{P}^i \underline{\lambda}^i$. These terms are square matrices in which each column is a vector \underline{P}^i multiplied by a constant $\underline{\lambda}^i$, and thus the resulting solutions are linearly de-

pendent. The solution matrix \underline{F}' therefore becomes numerically singular, and its resulting inverse can be of poor quality. Since the local form of the exchange potential is sensitive to the accuracy with which \underline{F}' (at the $n-1$ iteration) can be inverted, it is possible for these inaccuracies to ruin the outward propagation of \underline{F}' and thus prevent the convergence of Eq. (5). So far the only case in which we have experienced this problem is ${}^2\Sigma e\text{-LiH}$ scattering

2. I and OI methods

There are two main problems with these methods. The principal difficulty arises when the static or orthogonal static eigenphase sum lies on one side of $\frac{1}{2}\pi$ and the SE eigenphase sum lies on the other.

The methods in general have a slow monotonic convergence with iteration. For the special case above we see a convergence to $\frac{1}{2}\pi$ rather than the SE result. A qualitative explanation of this problem may be found by considering the single-channel case. For a phase shift of $\frac{1}{2}\pi$ the K matrix is infinite and so is the corresponding wave function. As the phase shift monotonically approaches $\frac{1}{2}\pi$, the K matrix grows larger and larger. Eventually a point is reached at which the K matrix is so large that the $K \cos(kR)$ term completely swamps the $\sin(kR)$ term in the wave function. The iterative procedure is unable at this point to switch branches of the tangent and, therefore, quadrants for the phase. In some cases this "quadrant-leaping" problem may be circumvented by changing the range of radial integration or by adding a model-exchange potential to the static potential; however, we have not as yet found a universal solution to it.

A second problem arises in the slow monotonic or oscillatory convergence with iteration. This requires us to take linear combinations of alternate solutions, as detailed by Coleman¹⁶ for atomic problems.

E. Method of solution

The coupled set of differential equations represented by Eqs. (7) and (9) are converted to a set of coupled integral equations. The integral equations are solved by an outward propagation scheme using a trapezoidal quadrature.¹⁷ We also employed a quadratic quadrature in the integration; however, we find no inherent advantage in going to this higher-order scheme.¹⁸ The linear independence of the scattering solution is enforced through the transformation procedures outlined in Sec. II B.

The most time-consuming part of the computation of the exchange term is the evaluation of the exchange integrals [see Eq. (2.21) of I]. Since

the integrals are labeled with only three of the six indices that determine the exchange term, they appear many times during its evaluation. Considerable savings in computational time can therefore be achieved by storing and sorting these integrals, so that they are evaluated only once. The actual integration is performed with a quadratic quadrature using the subroutine RS from the atomic R -matrix code.¹⁹

For a local potential we need only converge the cross sections or eigenphase sums with respect to the number of expansion terms in the continuum orbital, the number of moments in the multipole expansion of the local potential, and the asymptotic matching radius. In solving the SE equations, we must also guarantee the convergence of the exchange term with respect to the number of bound orbitals and the number of expansion terms in each bound and continuum orbital. We summarize our nomenclature for the five convergence parameters:

- (i) l_m , the maximum-order partial wave included in the spherical-harmonic expansion of the continuum orbital F ;
- (ii) λ_m , the maximum-order term retained in the Legendre expansion of the static potential (usually $\lambda_m = 2l_m$);
- (iii) l_m^{ex} , the maximum-order partial wave retained in the expansion of the continuum orbital in the exchange kernel;
- (iv) n_i^{ex} , the number of terms retained in the spherical-harmonic expansion of the i th bound target orbital in the exchange kernel;
- (v) r_m , the asymptotic matching radius.

For all our calculations we have included exchange with *all* bound orbitals. Exchanging with the most tightly bound orbitals (e.g., the $1\sigma_g$ and $1\sigma_u$ in N_2) seems essential only for accurately representing resonant continuum symmetries (e.g., Π_g in N_2 and Π in CO). We also find that for the four systems under consideration the number of expansion terms required to produce an accurate exchange kernel is smaller than that required to converge the continuum solution (i.e., $l_m^{\text{ex}} < l_m$). A similar result was found by Buckley and Burke⁶ for e - N_2 collisions. Except for resonant symmetries, two or three components in the expansion of the bound and continuum orbitals are usually sufficient to ensure a highly accurate exchange term. The number of terms that must be included in the expansion of the continuum orbital in order to converge the cross section is always at least a factor of 2 greater than needed to produce an accurate exchange term. The actual values of the convergence parameters are given for each system in Sec. III. One final point is worth noting. We find that the SE equations, especially when orthogonal-

ity is enforced, converge more rapidly in number of channels than the static case. While Morrison and Collins^{11(b)} found that for the static surface, $l_m = 24$ was needed to converge e - $N_2 \Sigma_g$ eigenphase sums to a few percent, we found that $l_m = 14$ is sufficient to converge the SE case to a comparable tolerance.

III. RESULTS AND DISCUSSION

A. Electron- H_2 scattering

Since H_2 is probably the most studied molecule within the SE approximation, we use it to illustrate some aspects of the iterative methods. The $H_2^1 \Sigma_g$ Hartree-Fock wave function of Fraga and Ransil²⁰ was used in all of the calculations. The internuclear separation is $R = 1.402a_0$, and the electronic energy and quadrupole moment given by this function are -1.1335 a.u. and $0.480ea_0^2$, respectively.

In Table I we compare the convergence with iteration for various methods of the $^2 \Sigma_g$ eigenphase sum at an energy of 2.0 Ry. It is clear from this table that the WFI and OWFI approaches converge much more rapidly than the I and OI schemes. The I and OI methods really require the use of acceleration schemes as described by Coleman¹⁶ to obtain reasonable convergence in number of iteration whereas the WFI and OWFI do not. Indeed, the I method diverges with iteration for Σ_g scattering for most energies below $k^2 = 2.0$ Ry. These patterns of behavior with iteration are followed closely for more complex target molecules, with the enforcement of orthogonality becoming increasingly important for reasonable convergence behavior.

Finally, for completeness we present in Table II single-center eigenphase sums and cross sec-

TABLE I. Convergence with iteration of $^2 \Sigma_g$ eigenphase sum (in radians) for e - H_2 scattering at an energy of $k^2 = 2.0$ rydbergs.

Iteration	WFI	OWFI	I	OI
0	0.9924	1.0398	0.9924	1.0398
1	1.2018	1.2761	1.2745	1.2147
2	1.2584	1.2766	1.2556	1.2516
3	1.2725	1.2766	1.2844	1.2654
4	1.2758	1.2766	1.2710	1.2713
5	1.2765	...	1.2797	1.2741
6	1.2766	...	1.2747	1.2754
7	1.2766	...	1.2778	1.2760
8	1.2759	1.2763
9	1.2770	1.2765
10	1.2764	1.2766
11	1.2768	1.2766
12	1.2765	...
15	1.2766	...

TABLE II. Static-exchange eigenphase sums (in radians) and cross sections (α_0^2 ; in parentheses) for e - H_2 scattering. Results are converged to better than 1%.

k^2 (Ry)	${}^2\Sigma_g$	${}^2\Sigma_u$	${}^2\Pi_g$	${}^2\Pi_u$	${}^2\Delta_g$
0.01	2.9303 (56.468)	0.0134 (0.207)	0.0012 (0.005)	-0.0025 (0.032)	-0.0020 (0.012)
0.04	2.7246 (53.034)	0.0493 (0.676)	0.0038 (0.006)	0.0045 (0.010)	-0.0034 (0.013)
0.09	2.5276 (47.896)	0.1233 (1.940)	0.0070 (0.007)	0.0262 (0.140)	-0.0043 (0.012)
0.16	2.3399 (41.823)	0.2459 (4.387)	0.0110 (0.010)	0.0642 (0.536)	-0.0044 (0.009)
0.25	2.1679 (35.483)	0.4084 (7.583)	0.0169 (0.015)	0.1155 (1.164)	-0.0031 (0.006)
0.36	2.0114 (29.467)	0.5797 (10.10)	0.0252 (0.026)	0.1729 (1.843)	0.0001 (0.003)
0.49	1.8729 (24.053)	0.7269 (10.95)	0.0363 (0.044)	0.2289 (2.370)	0.0054 (0.001)
0.64	1.7509 (19.427)	0.8361 (10.45)	0.0501 (0.068)	0.2779 (2.645)	0.0128 (0.003)
1.00	1.5509 (12.481)	0.9591 (8.092)	0.0840 (0.131)	0.3481 (2.554)	0.0324 (0.002)

tions for the lowest six symmetries at energies from 0.01 to 1.0 Ry for the OWFI method. These results are converged to much better than 1% in all parameters and should serve as a standard for future work. The convergence parameters are given in our earlier Letter.⁹

B. Electron- N_2 scattering

In a previous paper we reported results of our calculations on e - N_2 scattering in the ${}^2\Pi_g$ symmetry using the WFI method with various N_2 target-state wave functions. Here we present WFI results for all Σ , Π , and Δ scattering symmetries using the most accurate N_2 wave function available to us, namely, that of Cade, Sales, and Wahl.²¹ Eigenphase sums and cross sections are given in Table III together with the parameters that were required to converge these results to better than 5%. Except for the Π_g resonance symmetry, our results agree to 10% or better with those produced by Buckley and Burke⁶ with a non-iterative, single-center close-coupling method. The small differences can probably be attributed to the different target wave functions employed (Nesbet

TABLE III. Static-exchange eigenphase sums (in radians mod π) and cross sections (α_0^2 ; in parentheses) for e - N_2 scattering using the target wave function of Cade, Sales, and Wahl at $r_m = 85a_0$.

k^2 (Ry)	${}^2\Sigma_g$	${}^2\Sigma_u$	${}^2\Pi_g$	${}^2\Pi_u$	${}^2\Delta_g$	${}^2\Delta_u$
0.001	3.057 (89.35)	...				
0.01	2.874 (87.35)	3.119 (0.76)				
0.05	2.544 (77.20)	3.038 (2.48)				
0.1	2.311 (66.67)	2.937 (4.81)	0.011 (0.93)	-0.075 (1.20)	0.013 (0.08)	-0.004
0.2	2.011 (50.60)	2.749 (8.69)	0.202 (55.77)	-0.189 (3.82)	0.030 (0.18)	-0.004
0.3	1.808	2.584 (11.23)	1.461 (82.99)	-0.290	0.057 (0.36)	-0.003
0.4	1.654 (31.12)	2.440 (12.71)	2.316 (33.29)	-0.379 (8.00)	0.091 (0.63)	
0.5	1.524 (25.13)	2.316 (13.42)	2.454 (19.69)	-0.455 (10.43)	0.132 (1.00)	0.005 (0.01)
0.75	1.263 (15.87)	2.073 (13.24)	2.484 (12.14)	-0.601 (11.34)	0.247 (2.14)	0.026 (0.05)
1.0	1.043 (11.04)	1.908 (11.90)	2.453 (9.94)	-0.694 (12.05)	0.361 (3.24)	0.057 (0.12)
Parameters						
l_m	14	15	14	15	14	13
λ_m	28	30	28	30	28	26
l_m^{ex}	2	3	4	3	4	5
n_1^{ex}	2	2	2	2	2	2

as opposed to Cade, Sales, and Wahl). The more pronounced disagreements in the resonance symmetry are a result of our inclusion of exchange with the tightly bound $1\sigma_g$ and $1\sigma_u$ orbitals (neglected by Buckley and Burke). For the resonance symmetries in other molecules (CO and C_2), we have also verified that inclusion of exchange with *all* bound orbitals of the target molecule is necessary to obtain accurate cross sections. Given the differences in the methods and target wave functions, our results are in reasonably good agreement (10–15%) for all symmetries with those of the R -matrix^{3(a)} and T -matrix^{4(b)} calculations.

In Fig. 1 we show the effect of using various target wave functions on the resonant Π_g eigenphase sum. We use the near-Hartree-Fock wave function of Cade, Sales, and Wahl, (CSW),²¹ the extended-basis-set linear-combination-of-atomic-(molecular) orbitals self-consistent-field (LCAO-MO SCF) function of Nesbet (N),²² and the minimum-basis-set LCAO-MO SCF function of Ransil (R).²³ The total energies of these functions are -108.9928 , -108.9714 , and -108.5736 a.u., respectively. The corresponding quadrupole moments are -0.935 , -0.882 , and $-1.896a_0$.² We note that rather poor resonance parameters can be obtained by using wave functions of minimum-basis-set quality.⁹ The differences are less striking in the nonresonance symmetries.

C. Electron-LiH scattering

LiH is a small heteronuclear molecule with a large permanent dipole moment of 6.0 D. The present calculations employ the near-Hartree-Fock wave function of Cade and Huo,²⁴ which gives a total energy of -7.987313 a.u. and a dipole moment of 6.002 D for $R_{eq} = 3.015a_0$. The eigenphase sums along with their convergence parameters are

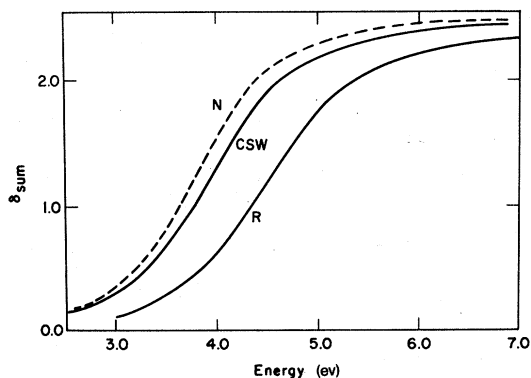


FIG. 1. Comparison of eigenphase sum as a function of energy for various choices of target wave function for $e-N_2\Pi_g$ collisions. The wave functions are as follows: Ransil (R), Nesbet (N), and Cade, Sales, and Wahl (CSW).

presented in Table IV for energies from 0.0025 to 1.0 Ry. The OWFI method had some difficulty with the ${}^2\Sigma$ symmetry when $l \geq 5$ were coupled. This was due to the inaccurate inversion of the F' matrix at small r values, as discussed in Sec. IID. Thus the ${}^2\Sigma$ results are produced with the OI method and the ${}^2\Pi$ results with the WFI method. The results are converged to much better than 5% with the parameters given in the table.

In Fig. 2 we present the static (S) and SE eigenphase sums for the Σ and Π symmetries. The S and SE results do not merge until approximately 3.0 Ry. We note that, in the Π symmetry at zero energy, the low-energy phase shift arises purely from the long-range dipole potential, and the Born approximation predicts the threshold phase shift correctly. The fact that the eigenphase sum at *low energies* approaches a value other than a multiple of π is an artifact of the fixed-nuclei approximation. For a polar system the integrated cross section, in the body-frame, fixed-nuclei approximation, summed over all channel indices l and m_l , is infinite. Thus the contribution from each symmetry is finite and nonzero (c.f., Ref. 25). Such problems with divergent cross sections can be avoided by use of a frame transformation to the space-fixed frame.²⁵⁻²⁸

D. Electron-CO scattering

Electron-CO scattering has been studied by previous authors within the static-exchange²⁸ and orthogonalized-static plus polarization approximations.²⁶ The present calculations use the near-Hartree-Fock CO wave function of McLean and Yoshimine²⁹ at the equilibrium internuclear sep-

TABLE IV. Σ and Π eigenphase sums (in radians) for e -LiH scattering using the target wave function of Cade and Huo.

k^2 (Ry)	${}^2\Sigma$	${}^2\Pi$	r_m
0.0025	6.2014	0.4295	225
0.01	5.1071	0.4538	225
0.04	4.1238	0.5318	155
0.1	3.4000	0.6739	100
0.16	3.0040	0.7807	100
0.25	2.6045	0.8961	100
0.49	2.0193	1.0895	100
0.81	1.6568	1.2403	100
1.0	1.5620	1.3004	100

Parameters			
l_m	7	6	
λ_m	14	12	
l_m^{ex}	2	3	
η_i^{ex}	3	3	

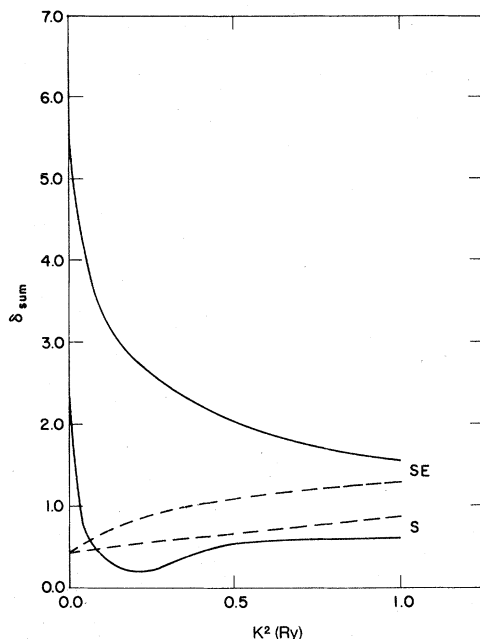


FIG. 2. Eigenphase sums as a function of energy for Σ (solid) and Π (dashed) e -LiH collisions in the static (S) and static-exchange (SE) approximations.

eration $R_{\text{eq}} = 2.132a_0$, which gives an energy of -112.78911 a.u. and a permanent dipole moment of 0.267 D.

In Table V we present our results for Σ and Π e -CO scattering. The values of the parameters used to obtain these results for the $\Sigma(\Pi)$ symmetry are as follows: $l_m = 7(9)$, $\lambda_m = 14(18)$, $l_m^{\text{ex}} = 2(4)$, $n_{l=6}^{\text{ex}} = 3(3)$, $r_m = 30.0(12.0)a_0$. We found that the resonance symmetry was especially sensitive to the choice of l_m^{ex} . The phase sum changed by

TABLE V. Static-exchange eigenphase sums (in radians mod π) and cross sections (a_0^2 ; in parentheses) for e -CO scattering.

k^2 (Ry)	Σ	k^2 (Ry)	Π
0.09	2.069 (81.22)	0.0735	0.016 (1.49)
0.16	1.675 (69.62)	0.1472	0.090 (7.72)
0.25	1.284 (58.42)	0.2205	0.459 (41.41)
0.36	0.906 (48.35)	0.2940	1.245 (88.26)
0.49	0.542 (39.73)	0.3675	1.678 (63.13)
0.64	0.193 (32.54)	0.441	1.803 (46.08)
		0.5879	1.810 (33.42)

a factor of two between $l_m^{\text{ex}} = 3$ and 4, whereas it changed by less than one percent when l_m^{ex} was increased to 5. A similar though not so dramatic sensitivity was observed in the convergence of the Π_g symmetry for e - N_2 collisions. Thus extreme care must be taken in close-coupling calculations in converging resonance symmetries. Nonresonance symmetries usually exhibit quite monotonic convergence in the various parameters.

In Fig. 3 we plot our eigenphase sums, together with those of Levin *et al.*²⁸ for Σ and Π e -CO collision symmetries. Considering the differences between target wave functions, we find excellent agreement between the two calculations at low energies. However, at higher energies the results of Levin *et al.* are consistently higher than ours. For the Π symmetry our resonance position is $E_{\text{res}} = 3.54$ eV and width $\Gamma = 2.07$ eV, as compared to $E_{\text{res}} = 3.4 \pm 0.1$ eV and $\Gamma = 1.65 \pm 0.15$ eV for Levin *et al.* Our Π resonance position and width are converged to better than 10%; the Σ results are converged to better than 5%.

IV. CONCLUSIONS

We have shown that iterative techniques are tractable and have broad application for the solution of the coupled equations involved in e -mole-

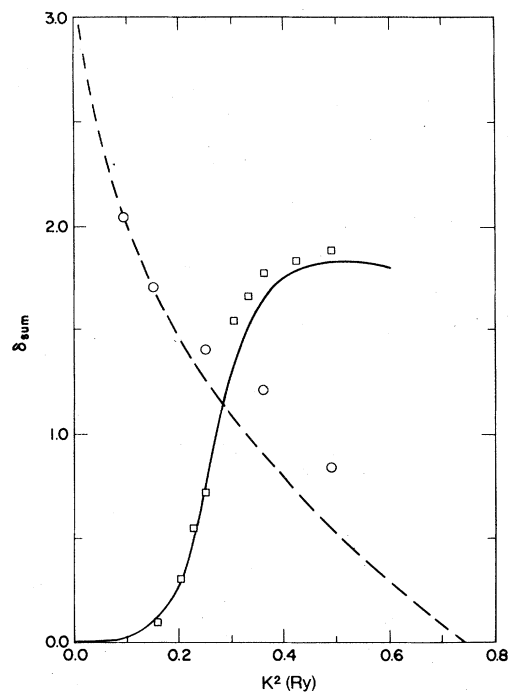


FIG. 3. Eigenphase sums as a function of energy for Σ (dashed) and Π (solid) symmetries for e -CO collisions. Comparison is made with the Σ (O) and Π (□) results of Levin *et al.* (Ref. 28).

cule scattering. In future papers we will investigate scattering within the SE approximation by other neutral molecules and extend our investigations to molecular ions and to the coupling of electronic states and the inclusion of bound $(n+1)$ -electron terms in the total wave function. In particular, we have found that the iterative techniques are more than competitive in terms of computation time with the L^2 basis-set techniques, and of course they have the property of showing uniform convergence in terms of all basic parameters.

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