LETTER TO THE EDITOR

Electronic excitation of the b $^3\Sigma_u$ state of H$_2$ by electron impact in the linear algebraic approach

B I Schneider and L A Collins

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Abstract. We have performed two-state close-coupling calculations on the X $^1\Sigma_g$ to b $^3\Sigma_u$ transition for e–H$_2$ scattering within the linear algebraic, effective optical potential approach. The strong orthogonality constraint between bound and continuum orbitals is relaxed by including correlation-type configurations. These correlation terms prove to be very important in the $^2\Sigma_g$ and $^2\Sigma_u$ symmetries and lead to an increase in the total cross section of a factor of two over earlier approaches, which neglected these terms. We obtain good agreement with recent R-matrix and Schwinger variational calculations.

The excitation of molecules by electron impact plays an important role in such diverse systems as the interstellar medium, planetary atmospheres and laser plasmas. In addition, the accurate representation of the scattering wavefunction is vital to the determination of photoionisation and free–free processes. To date, most excitation cross sections have been provided by the Born approximation or one of its derivatives such as the Ochkur–Rudge (Khare 1967, Cartwright 1970, Chung and Lin 1972, 1974). As in atomic scattering, impact parameter (Hazi 1981), distorted-wave (Fliflet and McKoy 1980, Fliflet *et al* 1979, Mu-Tao and McKoy 1982) and polarised orbital (Temkin and Vasavada 1967) methods have also been applied. The first application of the close-coupling technique occurred almost a decade ago (Chung and Lin 1978, Holley *et al* 1981, Weatherford 1980). While these calculations marked an improvement over earlier endeavours, they were rather restrictive in their scope, employing only a two-state approximation and neglecting the correlation terms needed to properly relax the orthogonality constraints. The last few years have witnessed the extension of three techniques, which proved very successful at the static-exchange level, to molecular excitation. The R-matrix (Burke *et al* 1977, Burke and Noble 1983, Tennyson and Noble 1985), the Schwinger variational (Takatsuka and McKoy 1981, 1984, Lima *et al* 1984) and the linear algebraic (Collins and Schneider 1983, 1984, Schneider and Collins 1983a, b) methods employ both analytical (L^2) and numerical bases in order to solve the multichannel Schrödinger equation for the scattering wavefunction from which cross sections can be extracted. So far, these techniques have been applied to simple molecular systems with the goal of establishing accurate and reliable sets of benchmarks among the various approaches.

To this end, and with particular reference to the accompanying letters by Baluja *et al* (1985) and by Lima *et al* (1985), we present calculations of excitation cross sections for the X $^1\Sigma_g$–b $^3\Sigma_u$ transition for electron scattering from H$_2$. This dipole-forbidden transition is particularly sensitive to the method employed since only a few

symmetries contribute to the total cross section and since the coupling is provided solely by the exchange terms. Our approach is based on a two-state close-coupling formulation in which correlation terms are included in order to relax the strong orthogonality constraint imposed on the bound and continuum orbitals. For this transition, the inclusion of these correlation terms is vital to obtaining accurate cross sections, as will be demonstrated by comparisons with the earlier two-state calculations (Chung and Lin 1978, Weatherford 1980). On the other hand, we obtain very good agreement with the R-matrix (Baluja *et al* 1985) and the recent Schwinger (Lima *et al* 1985) calculations.

We divide the letter into two additional sections. In the first section, we briefly review the theory of electronic excitation within the linear algebraic approach using an effective, separable optical potential. A preliminary report of this development appears in a recent letter (Collins and Schneider 1984) and a more comprehensive development will appear elsewhere (Schneider and Collins 1985). In the final section, we present the results of our two-state plus correlation calculations and compare them with other theoretical methods and with experiment.

The collision between an electron and a molecule of N electrons is characterised by a Schrödinger equation of the form

$$(H - E)\psi(1 \ldots N+1) = 0 \tag{1}$$

where

$$H = T + V_{eN} + V_{ee} + H_T \tag{2}$$

E is the total energy, and $\psi(1 \ldots N+1)$ is an $(N+1)$-electron wavefunction describing the total system (incident electron plus target). The wavefunction that corresponds to a particular state α of the N-electron target molecule is given by $\Phi_\alpha(1 \ldots N)$ and satisfies the eigenvalue equation

$$H_T\Phi_\alpha(1 \ldots N) = E_\alpha\Phi_\alpha(1 \ldots N). \tag{3}$$

The Coulombic interaction between the incident electron and the target electrons (nuclei) is represented by V_{ee} (V_{eN}), while the kinetic energy of the scattered electron is designated by T. We invoke the fixed-nuclei approximation (Temkin and Vasavada 1967) and freeze the molecule at its equilibrium separation.

We divide the total system wavefunction into two parts as

$$\psi(1 \ldots N+1) = A \sum_{\alpha=1}^{m} [\Phi_\alpha(1 \ldots N)F_\alpha(N+1)] + \sum_q d_q\chi_q(1 \ldots N+1) \tag{4}$$

where F_α represents the continuum orbital, A is an antisymmetry operator, and χ_q is an $(N+1)$-electron 'correlation' function. The summation in the first term is over a small number of states for which we directly seek scattering information; the A operator guarantees that the composite function obeys the Pauli principle for fermions. We impose the additional constraint that the bound orbitals (ϕ_i), which form Φ_α, and the continuum function F_α are orthogonal:

$$\int d\mathbf{r}\phi_i(\mathbf{r})F_\alpha(\mathbf{r}) = 0. \tag{5}$$

The second term in equation (4) represents a set of $(N+1)$-electron functions added to guarantee completeness. These functions play several roles. Their most common use is to relax the strong orthogonality condition of equation (5). For example, in

elastic, single-channel scattering of an electron by atomic hydrogen in the ^1S symmetry at the static-exchange level, the bound 1s and continuum ks orbitals are not in general orthogonal. If we force these orbitals to be so in the first term of (4), we must relax this constraint by adding a $1s^2(^1S)$ correlation function to the second term in order to obtain the correct result. The correlation term may also admit other functions, such as pesudostates, polarised orbitals, or excited-state configurations of the compound system, which represent higher-order corrections.

We derive the form of the scattering equations by employing the Feshbach (1958) projection operator description. We introduce the projection operators P and Q of the form

$$P\psi = \sum_{\alpha=1}^{m} A[\Phi_\alpha(1 \ldots N)F_\alpha(N+1)] \tag{6a}$$

$$Q\psi = \sum_q d_q\chi_q(1 \ldots N+1) \tag{6b}$$

and

$$P + Q = 1. \tag{6c}$$

We note that the continuum orbitals must also be orthogonal to the Q-space functions. We then insert these operators into equation (1) using the relationship (6c) and operate first with P and then with Q to derive the following two projection equations:

$$H_{PP}\psi_P + H_{PQ}\psi_Q = E\psi_P \tag{7a}$$

$$H_{QP}\psi_P + H_{QQ}\psi_Q = E\psi_Q \tag{7b}$$

where $H_{XY} \equiv \langle X|H|Y \rangle$ and $\psi_P(\psi_Q) \equiv P\psi(Q\psi)$.

By solving the second equation for ψ_Q and substituting the result into (7a) we obtain the usual optical potential form of the scattering equations

$$(H_{PP} + V_{\text{opt}})\psi_P = E\psi_P \tag{8}$$

where

$$V_{\text{opt}} = H_{PQ}(E - H_{QQ})^{-1}H_{QP}. \tag{9}$$

Since the details of the construction of the optical potential are given elsewhere (Schneider and Collins 1983a), we simply make a few observations. The optical potential form of equations (8) and (9) is merely a formal manipulation of the original Schrödinger equation. In order to form the optical potential, we approximate the continuum wavefunction that appears in equation (9) by a basis-set expansion in terms of known analytical functions, usually Gaussian-type orbitals (GTO). This approximation allows the optical potential to be generated independently of the solution of the scattering equation by standard configuration interaction (CI) molecular structure programs. This formulation produces a matrix or separable expansion of the optical potential and exchange terms. Such an expansion leads to simplifications in the scattering equations without loss of accuracy (Schneider and Collins 1981, Rescigno and Orel 1981).

The resulting scattering equations are reduced to a set of effective one-particle equations by multiplying through by the bound orbitals and integrating over the target coordinates $(r_1, \ldots, r_N)$. This reduction leads to a set of equations the solutions of which are the continuum orbitals $(F_\alpha(r_{N+1})|\alpha = 1, \ldots, m)$. We further reduce these equations by invoking a single-centre expansion of the bound and continuum orbitals

and by integrating over all angular coordinates. The resulting set of radial, coupled integrodifferential equations is solved by means of the linear algebraic (LA) technique (Schneider and Collins 1981, Collins and Schneider 1981) once a transformation is effected to the integral equations form. The linear algebraic approach, in which a discrete quadrature is introduced for the integrals, leads to a set of matrix equations, the solutions of which are the radial continuum functions. These matrix equations can be solved by standard linear systems techniques, which can be efficiently adopted to take full advantage of the vector and multitasking capabilities of the new generation of computers.

The LA equations for electronic excitation are typically of order $N_o(= n_s \times n_l \times n_p)$, which is the product of the number of states (n_s), the number of orbital angular momenta included within each state (n_l), and the number of radial mesh points (n_p). We observe that the size of the matrix equations can become rather large even for a small, few-state close-coupling calculation. However, in an earlier paper (Collins and Schneider 1984), we demonstrated that if the separable expansion of the optical potential is extended to the off-diagonal components of the direct or static terms, then the set of inelastic coupled equations reduces to a set of *elastic*, inhomogeneous equations of order $n_l \times n_p$. Thus, the problem of growing matrix size with increasing number of states is effectively circumvented. We are also experimenting with iterative schemes for solving the coupled direct part of the systems of equations, in the case where the separable approximation to the static coupling is poor, such as for dipole-allowed transitions. These techniques have so far proved quite efficient and lead to drastic reductions in storage since only parts of the full matrix need be considered at any time.

We present the results for the $X\,^1\Sigma_g$ to $b\,^3\Sigma_u$ transition for e–H_2 scattering. As pointed out before, this 'forbidden' transition offers a particularly sensitive test of the calculational prescription since, unlike the dipole-allowed transitions, only a few symmetries contribute to the total cross section and only the exchange terms lead to coupling. In addition, this transition has been studied by other theoretical methods, as well as by experiment (Khakoo *et al* 1985, Nishimura *et al* 1985).

We perform a two-state close-coupling calculation. The ground $X\,^1\Sigma_g$ state is represented by the configuration $1\sigma_g^2$ and the excited $b\,^3\Sigma_u$ state by $1\sigma_g 1\sigma_u$. The $1\sigma_g$ orbital is generated at the Hartree–Fock level while the $1\sigma_u$ orbital is constructed as an improved virtual orbital (IVO) appropriate to triplet coupling. The orbitals are expanded in an L^2 basis of GTO functions. This basis, which is employed in a standard set of molecular structure programs (Bobrowicz and Goddard 1977) to generate the orbitals and their properties, is given in table 1. In order to test the sensitivity of the cross sections to the basis, we have also employed the set of Lima *et al* (1984). We observe little sensitivity to this choice. The LA equations were solved using four orbital angular momenta per state $(n_l = 4)$ and a mesh of sixty points $(n_p = 60)$ covering the range from the origin to ten Bohr radii $(r_a = 10\ a_0)$. From this boundary outward, we assumed that only static, multipolar coupling was important. The resulting set of local coupled equations was integrated to a radius of 100 Bohr $(r_m = 100\ a_0)$ by the R-matrix propagator procedure of Light and Walker (1976). In order to relax the orthogonality constraint, we included, in the correlation part, terms of the form $1\sigma_g 1\sigma_u^2$ and $1\sigma_g^2 1\sigma_u$ for total scattering symmetries $^2\Sigma_g$ and $^2\Sigma_u$ respectively.

We also performed calculations in which the correlation terms were omitted but the orthogonality was still enforced, and obtained good agreement with the earlier calculations of Chung and Lin (1978) except in the $^2\Sigma_g$ symmetry. Our cross sections

Table 1. GTO basis set for e + H$_2$ calculations. exponential coefficients.

s-type	$R = \pm 1.4 \, a_0$

48.4479, 7.283 46, 1.651 39, 0.462 447, 0.145 885, 0.073, 0.0365

p$_z$-type	$R = \pm 1.4 \, a_0$

1.5, 0.5

s-type	$R = 0.0 \, a_0$

104.8576, 52.5228, 26.2144, 13.1072, 6.5536, 3.2768, 1.6384, 0.8192, 0.4096, 0.2048, 0.1024, 0.0512, 0.0256, 0.0128, 0.0064, 0.0032, 0.0016, 0.0008, 0.0004, 0.0002, 0.0001

p$_z$-type	$R = 0.0 \, a_0$

Same as above

d$_{z^2}$-type	$R = 0.0 \, a_0$

1.0, 0.333, 0.111, 0.037, 0.0123, 0.004

for this symmetry are almost an order of magnitude larger than theirs (0.125 a_o^2 compared with 0.0105 at 15 eV); however, since this symmetry makes only a small contribution to the total cross section, the overall results are in reasonably good agreement. In order to test this point further, we wrote a completely independent program, utilising the LA approach without the correlation contribution but with the orthogonality constraint. Thus, the formulation was the same as that of Chung and Lin (1978) and of Weatherford (1980). We obtained excellent agreement for *all* symmetries with our more general program.

In table 2 we present the partial and total cross sections for the X $^1\Sigma_g$ to b $^3\Sigma_u$ transition for two levels of approximation. Both calculations employ a two-state close-coupling (2CC) scheme. The first case we term the orthogonalised static exchange (OSE) in which (i) all direct and two-electron exchange terms are included, (ii) orthogonality is forced, and (iii) correlation terms are omitted. This scheme corresponds to the procedure described above and used by Chung and Lin (1978) and by Weatherford (1980). The second approach, which we term static-exchange plus correlation (SEC), includes the first two aspects of the OSE but incorporates correlation terms to relax the strong orthogonality constraint. We note that the cross section in the $^2\Sigma_g$ symmetry is almost a factor of five larger for the SEC case while in the $^2\Sigma_u$ symmetry the trend is nearly a factor of two. This leads to a total SEC cross section almost twice that of the OSE. Thus the importance of including correlation terms in such calculations

Table 2. Two-state close-coupling partial cross sections for the X $^1\Sigma_g$ to b $^3\Sigma_u$ transition in e-H$_2$ scattering in the OSE and SEC approximations. Incident electron energy (k^2) in Ryd and cross sections in a_0^2.

k^2	$^2\Sigma_g$		$^2\Sigma_u$		$^2\Pi_u$	$^2\Pi_g$	Total
	OSE	SEC	OSE	SEC	OSE	OSE	SEC
90.88203	0.0747	0.4772	0.4577	1.1330	0.0018	0.1553	1.9244
1.1025	0.1245	0.5157	0.4921	0.9952	0.0083	0.2825	2.0925
1.3230	0.1369	0.4797	0.4277	0.7533	0.0144	0.2840	1.8298
1.4700	0.1345	0.4297	0.3777	0.6152	0.0172	0.2565	1.5923
1.8376	0.1175	0.2978	0.2717	0.3793	0.0199	0.1766	1.0701
2.2051	0.0936	0.1937	0.1909	0.2422	0.0192	0.1162	0.7067

is amply demonstrated. The $^2\Pi$ cross sections are the same in both cases since no orthogonality terms arise in these symmetries. The contributions from the Δ symmetries are quite small at these energies.

In figure 1 we compare our total excitation cross section as a function of energy with those of the R-matrix method (Baluja *et al* 1985), the most recent Schwinger calculations (Lima *et al* 1985), and those of the earlier OSE calculations. We observe very good agreement with the R-matrix and Schwinger results, which also include correlation terms. We should note that the R-matrix calculations contain additional correlation functions, which are designed to improve the representation of the polarisation of the target and which are not included in the present LA or Schwinger cases. Finally, in figure 2, we compare our total cross section with the experimental results
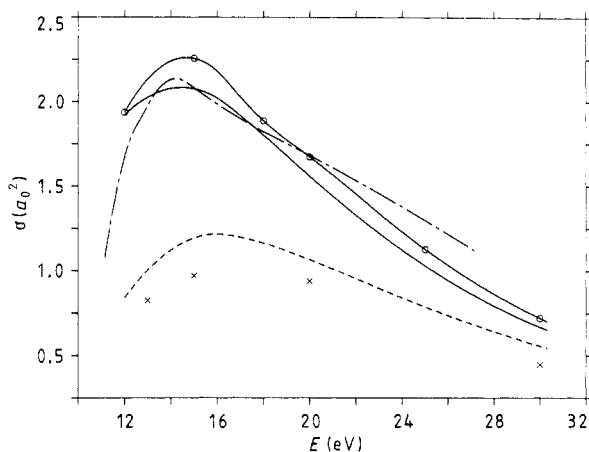

Figure 1. Comparison of theoretical calculations of the $X\ ^1\Sigma_g$-b $^3\Sigma_u$ total excitation cross sections as a function of incident electron energy for e–H_2 scattering. Nomenclature: full curve, present SEC calculations; broken curve, present OSE; chain curve, SEC (Baluja *et al* 1985); full curve with circles, SEC (Lima *et al* 1985); crosses, OSE (Holley *et al* 1981).
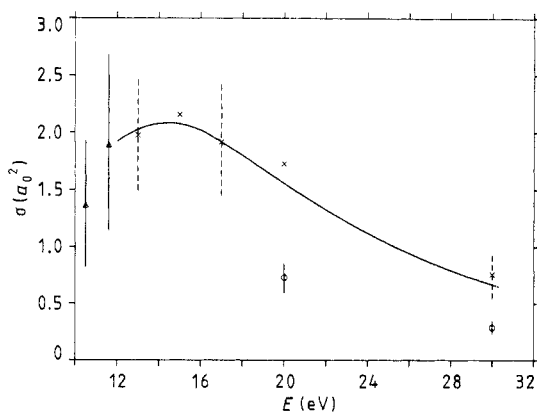

Figure 2. Comparison of theoretical and experimental $X\ ^1\Sigma_g$-b $^3\Sigma_u$ cross sections. Nomenclature: full curve, present SEC calculations; circles, experimental results (Khakoo *et al* 1985); crosses, experimental results (Nishimura *et al* 1985); triangles, experimental results (Hall and Andrić 1984).

of Khakoo *et al* (1985), of Hall and Andrić (1984) and of Nishimura *et al* (1985). We obtain very good agreement with Nishimura *et al* over the entire energy regime from 13 to 30 eV. In turn, our results are consistent with the data of Hall and Andrić (1984) at the lower energies. The exact role played by other excited states and by the opening of new inelastic thresholds will have to await further, more extensive calculations.

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