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Transition moments for excitation to Rydberg states of molecules using the *R*-matrix method: H_2 with $n \leqslant 5$

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Abstract. A method is presented for using scattering calculations performed with the *R*-matrix method to compute transition dipole moments between deeply bound and diffuse (Rydberg) states of molecules. The method is adapted from Seaton's atomic method. Results are presented for transitions of molecular hydrogen from the ground X $^1\Sigma_g^+$ to all the $^1\Sigma_u^+$ and $^1\Pi_u$ states with principal quantum number less than or equal to 5 as a function of internuclear separation ($1.0 \leqslant R \leqslant 3.0$ a_0). Comparisons are made with previous theoretical calculations, which do not extend beyond states with $n = 3$.

1. Introduction

The *R*-matrix method has been extensively used to calculate atomic radiative transition probabilities, for example in the opacity project (Seaton 1987, Berrington *et al* 1987). We have recently adapted the atomic methods of Seaton (1985) for calculating bound states of molecules (Sarpal *et al* 1991, Branchett 1991). In this paper we present the theory and calculations for molecular transition moments using the *R*-matrix theory. Again our approach is based on the work of Seaton (1985) but because of the difference between the long-range potentials of molecules as opposed to atoms it was necessary for us to use a different method of normalizing the wavefunctions.

Molecular hydrogen is a system of fundamental importance for both molecular physics and astronomy. A number of studies of high accuracy have been performed on allowed transitions of H_2 from its ground state to low-lying excited states using conventional quantum chemical techniques (for example Wolniewicz 1969, 1975, Dressler and Wolniewicz 1985, Bauschlicher and Langhoff 1991). These methods generally use large basis sets and extensive configuration interaction (CI) expansions. In the *R*-matrix approach, calculations of electron scattering from an N-electron target can be used to obtain bound states for an $(N + 1)$-electron system. In contrast to the conventional techniques these calculations are particularly good for diffuse or Rydberg states of the system. To our knowledge there has been one previous attempt to use a scattering calculation to predict transition moments in H_2. In this work Arrighini *et al* (1980) used the first Born approximation plus exchange to obtain oscillator strengths for transitions to the three lowest states of $^1\Sigma_u^+$ and $^1\Pi_u$ symmetry.

Excitation to high lying states is of interest both to support experimental studies (for example Davies *et al* 1990a,b) and for astrophysics. In this work we present

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transition energies and moments for H_2 from its X $^1\Sigma_g^+$ state to the six lowest states of both $^1\Sigma_u^+$ and $^1\Pi_u$ symmetry as a function of internuclear separation. These are compared with the previous theoretical results for transitions to the lower states.

2. Theory

Within the molecular R-matrix method space is divided into two regions separated by a sphere of radius a. This sphere is centred on the centre of mass of the N-electron molecule and is chosen to just enclose the molecular charge distribution. In the inner region the potential is strong and multicentred; exchange, correlations and polarization effects between target electrons and incident electrons must be considered. In the outer region exchange and correlation effects can be neglected and only the effects of the target moments and long-range polarization are included in the calculation. A detailed discussion of the R-matrix method for electron–molecule scattering is given by Gillan *et al* (1987) and only the points relevant to the calculation of transition dipole moments between bound states will be discussed.

In order to calculate the bound states of an $(N+1)$-electron system the wavefunction in the inner region ψ_k is represented by

$$\psi_k = \mathcal{A}\sum_{i,j}\phi_i(\boldsymbol{x}_1\ldots\boldsymbol{x}_N)u_{ij}(\boldsymbol{r})s(\sigma_{N+1})a_{ijk} + \sum_i \chi_i(\boldsymbol{x}_1\ldots x_{N+1})b_{ik} \qquad (1)$$

where $\mathcal{A}$ is the antisymmetrization operator and $\boldsymbol{x}_n = (\boldsymbol{r}_n, \sigma_n)$ is the space spin coordinate of the nth electron. The spatial coordinate of the $(N+1)$th electron is denoted by $\boldsymbol{r}$ and for convenience its space and spin functions separately identified. The functions ϕ_i represent the N-electron target functions and the functions u_{ij} are continuum orbitals expanded as a partial wave expansion of the radial part of the one-dimensional Schrödinger equation using a suitable potential and subject to the boundary conditions

$$u_{ij}(0) = 0 \qquad (2)$$

and

$$\mathrm{d}u_{ij}/\mathrm{d}r|_{r=a} = \beta u_{ij} \qquad (3)$$

where β is an arbitrary constant taken in this work as zero.

The functions χ_i represent configurations where all $N+1$ electrons are in target molecular orbitals and the second sum in equation (1) is therefore used to allow for short-range correlation and polarization effects between the scattered electron and the target molecule. The coefficients a_{ijk} and b_{ik} are found by diagonalizing the Hamiltonian matrix H_{N+1}

$$\langle\psi_k|\mathsf{H}_{N+1} + L_{N+1}|\psi_{k'}\rangle = e_k\delta_{kk'} \qquad (4)$$

where L_{N+1} is the Bloch operator used to ensure that the Hamiltonian operator is Hermitian.

From equation (1) one can define inner region reduced radial functions by (Gillan *et al* 1987)

$$F_i(r) = \langle \phi_i Y_{l_i m_i} | \psi_k \rangle. \tag{5}$$

On the boundary, $r = a$, and for normalized functions ψ_k, the reduced radial functions satisfy the equation (Seaton 1985)

$$F_i(r) = \sum_j R_{ij}(E) a \left(\frac{\mathrm{d}F_j}{\mathrm{d}r} - \beta F_j \right) \tag{6}$$

which defines the R-matrix. At the boundary, R_{ij} is given by the equation (Gillan *et al* 1987)

$$R_{ij}(E) = \frac{1}{2a} \sum_k w_{ik}(a)(e_k - E)^{-1} w_{jk}(a) + \delta_{ij} B_i. \tag{7}$$

The Buttle correction, B_i, is necessary because of the introduction of arbitrary boundary conditions, equation (2), and the functions $w_{ik}(a)$ are the surface amplitudes of the inner region wavefunctions, full details of which are given in Gillan *et al* (1987).

The total wavefunction of the system in the inner region Ψ_i can be expanded in terms of the complete set of functions ψ_k as

$$\Psi_K = \sum_k \psi_k C_{kK} \tag{8}$$

where the coefficients C_{kK} are referred to as the bound-state coefficients.

In the outer region the wavefunction at a particular energy, Ψ_j, must be matched to the inner region functions at the R-matrix boundary and, for bound states, must tend to zero as r tends to infinity. These Ψ_j can be expanded in terms of the target wavefunctions as

$$\Psi_j = \sum_{i,j} \phi_i \frac{1}{r} P_{ij}(r). \tag{9}$$

In our method, the outer region radial functions, P_{ij}, are calculated by first using an asymptotic Gailitis expansion (Noble and Nesbet 1984) at an appropriate radius and then propagating inwards numerically using the Runge–Kutta–Nystrom method (NAG library routine D02LAF).

By imposing suitable boundary conditions Seaton (1985) showed that the condition for a bound state to exist is given by the equation

$$\sum_j P_{ij} - \left[\sum_k R_{ik}(E) \left(\frac{\mathrm{d}P_{kj}}{\mathrm{d}r} - \beta P_{kj} \right) \right] X_j = 0 \tag{10}$$

where all the functions are evaluated at the R-matrix boundary. The eigenvector X_j can then be used to calculate the bound-state coefficients using the equation

$$C_{kK} = \sum_i \frac{w_{ik}}{(e_k - E)} \sum_j \left(\frac{\mathrm{d}P_{ij}}{\mathrm{d}r} - \beta P_{ij} \right) X_j. \tag{11}$$

A systematic method of searching for these bound states, based on Seaton's method (1985), has been discussed in detail in Sarpal *et al* (1991).

In the inner region the normalization integral is given by (Seaton 1985)

$$\langle\Psi_K|\Psi_K\rangle_{\mathrm{I}} = \sum_m \sum_l \left(\frac{\mathrm{d}F_m}{\mathrm{d}r} - \beta F_m\right) \frac{\mathrm{d}R_{ml}}{\mathrm{d}E} \left(\frac{\mathrm{d}F_l}{\mathrm{d}r} - \beta F_l\right). \tag{12}$$

This equation may be rewritten, using the matching conditions at the R-matrix boundary

$$F_i = \sum_j P_{ij} X_j \tag{13}$$

and

$$\frac{\mathrm{d}F_i}{\mathrm{d}r} = \sum_j \frac{\mathrm{d}P_{ij}}{\mathrm{d}r} X_j \tag{14}$$

as

$$\langle\Psi_K|\Psi_K\rangle_{\mathrm{I}} = \sum_i \sum_j X_i Y_{ij} X_j \tag{15}$$

where Y_{ij} is given by

$$Y_{ij} = \sum_m \sum_l \left(\frac{\mathrm{d}P_{mi}}{\mathrm{d}r} - \beta P_{mi}\right) \frac{\mathrm{d}R_{ml}}{\mathrm{d}E} \left(\frac{\mathrm{d}P_{lj}}{\mathrm{d}r} - \beta P_{lj}\right) \tag{16}$$

where the energy derivative of **R** can be calculated analytically. In the outer region the normalization integral is given by

$$\langle\Psi_K|\Psi_K\rangle_{\mathrm{O}} = \sum_i \sum_j X_i N_{ij} X_j \tag{17}$$

where N_{ij} is given by

$$N_{ij} = \sum_n \int_a^\infty P_{ni} P_{nj} \,\mathrm{d}r. \tag{18}$$

The complete normalization integral is then given by

$$\langle\Psi_K|\Psi_K\rangle = \sum_i \sum_j X_i (N_{ij} + Y_{ij}) X_j \tag{19}$$

which can be normalized to unity on taking X_i to be normalized by

$$\sum_i \sum_j X_i (N_{ij} + Y_{ij}) X_j = 1. \tag{20}$$

In Seaton's atomic method (1985), the outer region functions were chosen so that the functions N_{ij} satisfied the equation

$$N_{ij} = \delta_{ij} . \tag{21}$$

However, for the molecular case, the outer region functions have to be of a more complex form in order to adequately represent such long-range effects as the potential due to the target multipole moments. The functions N_{ij}, therefore, had to be calculated by integrating numerically in the asymptotic region and the propagation region and adding these contributions.

Within the dipole length approximation the transition dipole in the inner region for going from state ψ_k to state ψ'_k is given by

$$\mathcal{T}_{kk'} = \left\langle \psi_k \left| \sum_{i=1}^{N+1} e_i r_i \right| \psi'_k \right\rangle_{\mathrm{I}} . \tag{22}$$

If one neglects the contribution to the transition dipole from the wavefunctions in the outer region (Seaton 1981, 1986) then, from equation (8), the dipole $t_{KK'}$ for a transition from state K with energy E_K to state K' with energy $E_{K'}$ is given by

$$t_{KK'} = \left\langle \Psi_K \left| \sum_{i=1}^{N+1} e_i r_i \right| \Psi'_{K'} \right\rangle = \sum_{kk'} C_{kK} \mathcal{T}_{kk'} C_{k'K'} . \tag{23}$$

From the transition dipole the oscillator strength $f_{KK'}$ can then be calculated using the definition, in atomic units, of Schadee (1978)

$$f_{KK'} = \frac{2}{3} \frac{(2 - \delta_{0,\Lambda+\Lambda'})}{(2 - \delta_{0,\Lambda})} (E_{K'} - E_K) |t_{KK'}|^2 . \tag{24}$$

3. Results and discussion

R-matrix calculations for electron–H_2^+ scattering were based on the study of super-excited Rydberg states of H_2 by Shimamura *et al* (1990). The H_2^+ target was represented by atom-centred Slater type orbitals (STOs) for which exponents had been optimized for each internuclear separation. For the σ orbitals we used the (1s,2s,2p) exponents optimized by Shimamura *et al* (Shimamura 1991), who optimized for g and u symmetry combinations separately. For the π orbitals we used the (2p,3p,3d) exponents optimized by Cohen and Bardsley (1980) for the lowest $^2\Pi_u$ state of H_2^+. Our target basis thus consisted of three orbitals for each of $\sigma_g, \sigma_u, \pi_u$ and π_g symmetry types.

Scattering calculations were performed using a close-coupled expansion comprising the lowest three states of H_2^+ (X $^2\Sigma_g^+$, A $^2\Sigma_u^+$ and B $^2\Pi_u$) and an R-matrix radius, a, of 14 a_0. The H_2^+ target functions were augmented by numerical functions with $\ell \leqslant 6$ and $m = 0$ or 1 and energy below 7 Ryd (Gillan *et al* 1987). These functions were Lagrange orthogonalized to the lowest target orbitals of σ_g, π_u and π_g symmetry (Tennyson *et al* 1987). Calculations were performed for hydrogen bondlengths of $R = 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, 2.8$ and $3.5\ a_0$. The inner region wavefunction also contained all symmetry allowed configurations obtained by placing all three electrons in the target orbitals (the second sum in (1)). The outer region potential was given by all diagonal and off-diagonal dipole and quadrupole moments.

Extensive comparisons were performed with the ${}^1\Sigma_g^+$ resonance positions and widths of Shimamura *et al* (1990). Our results were generally in good agreement with theirs although our resonance positions were all shifted to slightly lower energy and resonance widths tended to be narrower. This effect is directly attributable to our better representation of Π polarization effects by the inclusion of the B ${}^2\Pi_u$ state in our close-coupled expansion and the use of a more extensive π basis set for the H_2^+ target.

Bound states were found using the method of Sarpal *et al* (1991) described earlier. A Gailitis expansion was used at $30\ a_0$ and the wavefunctions propagated inwards by direct numerical integration of the differential equations. With this method we obtained energies and eigenfunctions for the ground state and lowest six states of both ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ symmetry. The energies of these excited states, which cover all the Rydberg states up to $5n$, are given in table 1. A quantum defect analysis (Seaton 1983) readily showed that the states were comprised of an np series with quantum defects ($= n - \nu$) of approximately 0.073 and −0.066 for ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ respectively, and an nf series with a quantum defect of about 0.005 for both symmetries. Table 1 also gives values of ν^3f which should, and indeed was found to, be slowly varying (Burgess and Seaton 1960). This, approximately n independent, form of the transition moment was found to be particularly helpful as it behaved very erratically when our wavefunctions were not correctly normalized.

Table 1. Bound state energies, E, effective quantum numbers ν, transition dipoles, μ, and oscillator strengths, f, for excitation from the ground state to the lowest lying ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ of H_2 at the fixed equilibrium internuclear separation of $1.4\ a_0$. The fraction of the wavefunction in the inner region, I, and the function $\nu^3 f$ are also shown. The assignments to atomic configurations $1sn\ell$ are based on effective quantum numbers of the excited states.

State	$E(E_h)$	ν	I	μ (au)	f	$\nu^3 f$	$n\ell$
${}^1\Sigma_g^+$	−1.168 391	(0.9135)	1.0000				
${}^1\Sigma_u^+$	−0.703 953	1.9266	0.9995	−0.9834	0.2995	2.1414	2p
	−0.627 599	2.9272	0.8232	0.4091	0.0603	1.5120	3p
	−0.601 673	3.9267	0.2781	−0.3059	0.0353	2.1376	4p
	−0.600 569	3.9953	0.2549	−0.2952	0.0330	2.1008	4f
	−0.589 849	4.9263	0.1302	0.2223	0.0191	2.2770	5p
	−0.589 291	4.9943	0.1386	0.2297	0.0204	2.5362	5f
${}^1\Pi_u$	−0.686 564	2.0644	0.9986	−0.7390	0.3508	3.0869	2p
	−0.622 402	3.0670	0.7259	0.3542	0.0913	2.6364	3p
	−0.600 555	3.9962	0.3366	−0.2846	0.0613	3.9084	4f
	−0.599 491	4.0659	0.2887	−0.2654	0.0534	3.5926	4p
	−0.589 281	4.9956	0.1388	0.1986	0.0305	3.7943	5f
	−0.588 742	5.0641	0.1356	0.1970	0.0300	3.8980	5p

Table 1 also gives the fraction of the wavefunction of the $(N+1)$th (i.e. second) electron that is found inside the R-matrix sphere of $14\ a_0$. This was actually calculated by using the properties of the wavefunction of this electron outside the sphere as in this region the wavefunction of the 'scattering' electron can be unambiguously identified (see section 2). It can be seen that the ground state is effectively confined within the R-matrix sphere; therefore, for transitions involving the ground state, the contributions to the transition moments from the outer region can be safely neglected.

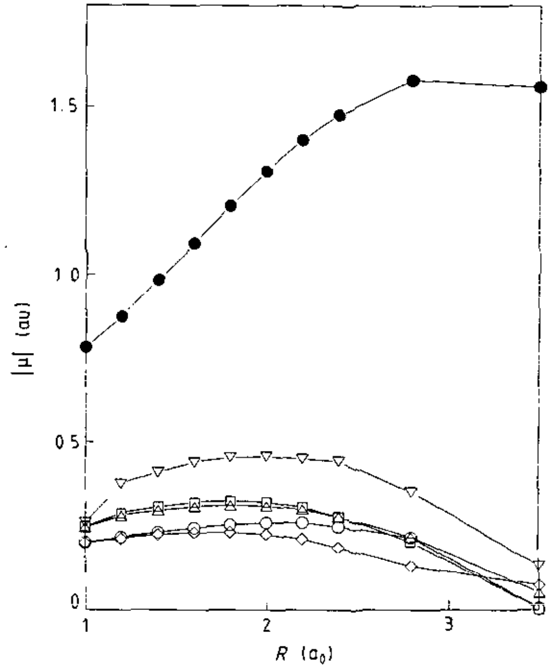

Figure 1. Transition dipoles in au as a function of internuclear separation, in a_0, for excitation from the ground to the first six excited ${}^1\Sigma_u^+$ states of H_2: full circle, first state; open inverse triangle, second state; open square, third state; open triangle, fourth state; open diamond, fifth state; open circle, sixth state.

One problem with our method is that it is difficult to unambiguously determine the sign of transition moments. This is because the the coefficients of the ψ_k (see equation (1)) are only determined by diagonalization of the Hamiltonian matrix to within a phase factor. As the intensity depends on the square of the moment this is annoying rather than serious. However when generating transition moments as a function of H_2 bondlength, R, we avoided arbitrary changes of sign by considering $|\mu|$ only. Figures 1 and 2 give results for $|\mu(R)|$ for transitions from X ${}^1\Sigma_g^+$ to states with ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ symmetry respectively.

Tables 2 and 3 compare our results with previous *ab initio* calculations. Table 2 tabulates the most accurate results available from conventional electronic structure calculations. These calculations only cover the lowest two transitions in each symmetry, for which our results are probably least accurate (Sarpal *et al* 1991). Our transition dipoles agree with these accurate estimates to about 5%. Also shown are the associated transition energies. Our transition energies agree to about 1% or 0.005 E_h. This agreement is similar to the error in our X ${}^1\Sigma_g^+$ ground state energy for which we obtain -1.1684 E_h compared with an effectively exact value of -1.1745 E_h (Kolos and Wolniewicz 1965). The error in our H_2^+ ground state

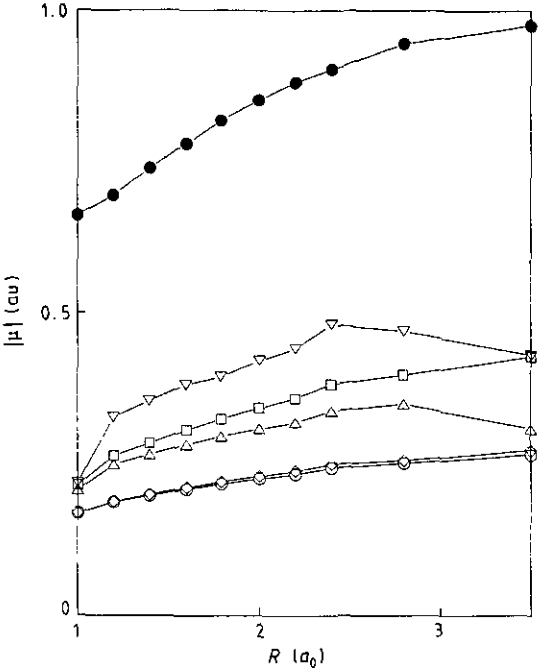

Figure 2. Transition dipoles in au as a function of internuclear separation, in a_0, for excitation from the ground to the first six excited ${}^1\Pi_u$ states of H_2: full circle, first state; open inverse triangle, second state; open square, third state; open triangle, fourth state; open diamond, fifth state; open circle, sixth state.

Table 2. H_2 transition dipoles in atomic units for excitation from the ground state to the lowest lying ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ states of H_2 at $R = 1.4\ a_0$. Dipoles (in au) calculated using the length and velocity approximation are denoted μ_L and μ_V respectively. The excitation energies ΔE are given in Hartree.

State	Previous Theory		Bauschlicher and Langhoff (1991)			Present work	
	ΔE	μ_L	ΔE	μ_L	μ_V	ΔE	$\lvert\mu_L\rvert$
${}^1\Sigma_u^+$	0.4688[a]	0.9821[d]	0.4686	0.9802	0.9796	0.4644	0.9834
	0.5459[b]	0.3966[b]	0.5455	0.3973	0.3971	0.5408	0.4091
${}^1\Pi_u$	0.4862[c]	0.7432[d]	0.4866	0.7212	0.7170	0.4818	0.7390
			0.5510	0.3324	0.3302	0.5460	0.3542

[a] Kołos and Wolniewicz (1968).
[b] Wolniewicz (1975).
[c] Rothenberg and Davidson (1966).
[d] Dressler and Wolniewicz (1985).

energies was 0.001 E_h or less. It is likely that the major source of error in our H_2 energies is due to underestimating electron correlation effects. These could only be accounted for by using larger STO basis sets.

It is interesting to note that, at least about the H_2 equilibrium geometry, transitions to p and f states with the same n and symmetry are very similar in intensity.

Table 3. Oscillator strengths, f, for excitation from the ground state to the lowest lying $^1\Sigma_u^+$ and $^1\Pi_u$ states of H_2 at $R = 1.4\ a_0$. The excitation energies ΔE are given in Hartree.

State	Arrighini		Present work	
	ΔE	f	ΔE	f
$^1\Sigma_u$	0.4678	0.2907	0.4644	0.2995
	0.5427	0.0611	0.5408	0.0603
	0.5685	0.0207	0.5667	0.0353
			0.5678	0.0330
$^1\Pi_u$	0.4852	0.3492	0.4818	0.3508
	0.5486	0.0940	0.5460	0.0913
			0.5678	0.0613
	0.5717	0.0427	0.5689	0.0534

This is in contrast to the atomic case where the $\Delta\ell = 1$ transition is strongly favoured and is a reflection the 'inner region' nature of the transition from the ground state. A study of Rydberg–Rydberg transitions in HeH showed that they can be well described using the appropriate atomic transition moments (Sarpal and Tennyson 1992).

Table 3 compares our oscillator strengths with those obtained by Arrighini *et al* (1980) who also used a scattering calculation but in their case based upon the first Born approximation. The agreement with Arrighini *et al* is reasonable for the lower two transitions of each symmetry. However for transitions to the $4n$ level the results of Arrighini *et al* appear significantly less accurate. This is almost certainly due to the omission of any f functions from their basis set.

4. Conclusions

We present a formulation for calculating bound–bound transition moments based on the atomic R-matrix method of Seaton (1985). This formulation is general for any diatomic molecule. However for accurate results to be obtained for diatomics with many (N) electrons it will be necessary to use accurate wavefunctions for the $(N-1)$-electron target. Scattering calculations have been performed using the molecular R-matrix method and correlated target wavefunctions (e.g. Branchett and Tennyson 1990), but further work will be required improving the computational algorithms before these target wavefunctions can approach the accuracy routinely used in standard quantum chemical calculations.

Results are presented for transitions from the ground state of molecular hydrogen as a function of internuclear separation. These results agree well with the available results for the lower transitions and augment these by presenting results to states for which no previous *ab initio* results are available.

The present method is only reliable for transitions where one or both of the states involved are confined within the R-matrix sphere. It is thus not applicable to transitions between Rydberg states such as the H_2 5g–4f, 6h–5g and 8i–6h systems observed recently by Davies *et al* (1990). Our plan is to include the outer region contribution to our transition moments for bound–bound and bound–free (Tennyson *et al* 1986, Tennyson 1987) transitions by adapting the atomic methods of Seaton (1981, 1986) to molecules.

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