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LETTER TO THE EDITOR

Electronic transitions in the HeH molecule: a MQDT approach

Baljit K Sarpal and Jonathan Tennyson

Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

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Abstract. We make use of multichannel quantum defect theory (MQDT) to calculate the eigenvectors of the bound states of HeH. By making use of expressions for Coulomb transition dipoles and simple angular momentum algebra we calculate transition probabilities for several states of HeH. These results are in general agreement with previous *ab initio* determinations where available but also show considerable structure in dipole moments arising from mixing of states near avoided crossings.

The electronic transition moments of the various excited states of molecules are very important in both observing and assigning molecular spectra. Knowledge of the energy levels of the molecule are often not sufficient for this purpose as vibrational and rotational motion results in transitions from several excited electronic states in the same spectral region. This problem is further exacerbated when the electronic states themselves are not accurately known. In such cases transition moments provide additional information so that the spectrum can be simulated and compared with experiment.

The *R*-matrix method has been shown to be particularly adept at calculating excited bound states of both atoms (Seaton 1985, Berrington and Seaton 1985) and molecules (Sarpal *et al* 1991a). In particular this method yields very accurate transition energies between the excited states. Once the bound states are determined one can use matrix elements of the dipole operator determined from standard quantum chemistry codes to give the transition dipole moment (TDM) (Branchett and Tennyson 1992).

In this letter we report a much simpler method of calculating TDM, based on the scattering framework and extrapolating below threshold to the bound state region. This approach is particularly suited to those molecules, like the HeH molecule, which have excited states composed of a compact core with a diffuse Rydberg electron. This method does not allow interaction between Rydberg series converging to different thresholds; it will thus work best for simple cases such as those where the core excited states lie above the first ionization threshold.

We apply our method to the case of HeH for which *ab initio* calculations have been made previously (Theodorakopoulos *et al* 1987, Petsalakis *et al* 1987). This molecule has been extensively studied experimentally by Ketterle (1989, 1990a, b, c, d).

If one separates between a compact core and a single active Rydberg electron then the wavefunction of the Rydberg electron is naturally expanded as a sum of partial waves. The transition dipole between two Rydberg states, assuming that core electrons do not take part in the transition, can be expressed as

$$d_{i\to f}=(-1)^{\Lambda_f}\sum_{l_il_f} c_{l_i}c_{l_f}[(2l_i+1)(2l_f+1)]^{1/2}\begin{pmatrix} l_f & 1 & l_i \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_f & 1 & l_i \\ -\Lambda_f & q & \Lambda_i \end{pmatrix}\int_0^\infty P_{l_i} r P_{l_f}\,\mathrm{d}r \qquad (1)$$

where we have explictly assumed that spin is a good quantum number. The 3-j symbols contain all the information concerning angular dependence. The parameter q is the component of the dipole operator having the values 1, 0 and −1 and Λ_i and Λ_f are the symmetries (projection of the total angular momentum on the nuclear axis) of the initial and final states respectively. The summation over orbital angular momentum simply reflects the fact that diatomic molecules are not spherically symmetric in general. In the integral, P_l are the radial wavefunctions of the electron undergoing the transition. Generally a very large partial wave expansion, up to $l \sim 20$, is required to obtain good representation of the electron wavefunction, due to the singularities at the nuclei. As the major contribution to the TDM between Rydberg states arises from larger distances a much smaller partial wave expansion for the wavefunction suffices.

Recently Kaufmann (1991) has treated transitions for NO with a method very similar to that presented here. The difference lies in the way the mixing coefficients have been obtained. He explicitly determined the wavefunction of the Rydberg electron and then projected the wavefunction onto spherical harmonics to obtain the coefficients of the partial wave expansion. We follow a somewhat different approach based on the scattering formalism.

Scattering calculations on the ion and an electron yield the reactance K matrix which can be diagonalized to give the phaseshifts δ_l, where channel label l corresponds to the dominant angular momentum. The corresponding eigenvectors of the K matrix give the mixing coefficients between the open channels. If the K matrix is calculated at a sufficiently low energy then the phaseshifts above the threshold correspond to quantum defects of the bound states below that threshold, i.e.

$$\delta_l = \pi\mu_l. \qquad (2)$$

More precisely $\delta(E)$ is an analytic continuation of $\pi\mu(E)$ across a threshold (Seaton 1983).

In the absence of energy localized interactions, for instance due to core excited states, it is reasonable to assume that the l composition of the scattering eigenchannels is the same as those of the bound states. The coefficients of the K-matrix eigenvector then correspond to the mixing coefficients, c_l, of the bound states in (1).

The only other information required to calculate the TDM is the radial integral in (1). For sufficiently excited states of the neutral molecule these can be approximated by the Coulomb dipole integrals which are obtained by linear interpolation of tables given by Bates and Damgaard (1949). To summarize, the wavefunction of the active electron in all space is expressed as a linear combination of Coulombic wavefunctions where the coefficients of the expansion are the mixing coefficients determined from the scattering calculations.

The scattering problem was treated using the molecular R-matrix method described in detail by Gillan *et al* (1987). Details of the e–HeH$^+$ scattering calculations can be found in Sarpal *et al* (1991b). The calculations were carried out on a grid of geometries, $R = 1.0$, 1.2, 1.3, 1.4, 1.455, 1.5, 1.6, 1.8, 2.0, 2.4, 2.8, 3.0, 4.0 a_0.

In table 1 we give the l composition of the six channels retained for Σ symmetry states and five channels for the Π symmetry states at $R = 1.5$ a_0. Note that these mixing coefficients are strictly valid for high Rydberg states, $n \geqslant 5$, and the states which are

Table 1. Quantum defects and eigenvector composition for (a) $^2\Sigma$ and (b) $^2\Pi$ symmetry at $R = 1.5a_0$.

Quantum defect	Eigenvector composition					
	$l=0$	1	2	3	4	5
(*a*) $^2\Sigma$						
0.106	0.95	0.30	−0.14			
−0.456	−0.31	0.94	−0.11			
0.029	0.10	0.14	0.98	0.09		
0.009	−0.01	−0.01	−0.07	0.83	0.53	0.15
0.003	0.01	0.01	0.04	−0.53	0.70	0.47
−0.004			−0.01	0.14	−0.47	0.87
(*b*) $^2\Pi$						
0.044		0.96	−0.29	0.01		
0.017		0.29	0.93	0.21	0.03	−0.01
0.007		−0.06	−0.17	0.74	0.62	0.19
0.002		0.04	0.10	−0.61	0.61	0.49
−0.004		−0.01	−0.03	0.19	−0.49	0.85

dominantly high l partial waves are probably not fully converged due to truncation of the partial wave series at $l = 5$. Comparing the multichannel quantum defects (MQD), calculated at 0.001 Ryd above the ground state of HeH^+, with quantum defects calculated from the bound states (Sarpal *et al* 1991a) shows that even for the lowest bound states the agreement is very good, within ±0.002. We give the MQD as a function of R for the two symmetries in figure 1.

No two curves of the same total symmetry can cross, thus figure 1 shows several avoided crossings. Whether a diabatic or an adiabatic model is appropriate is not obvious from our calculations as we do not evaluate the coupling matrix elements. In figure 1 the adiabatic states are indicated by full curves and the diabatic states by symbols. In table 2 we give the TDM for various transitions as a function of internuclear separation. When calculating these TDM we have retained only those partial waves with $l < n$. This ensures that avoided crossings which occur for states with large n do not appear spuriously for smaller n. An example of this is the A state, a member of the $ns\,^2\Sigma$ series, which has no curve crossings but higher members of this Rydberg series have a crossing with the $nd\,^2\Sigma$ series (see figure 2 of Sarpal *et al* 1991a). One needs to be careful not to use this reduced partial wave expansion too freely as real avoided crossings would also be smoothed over. In general we find that to get a good description of a state of particular angular momentum, especially near curve crossings or at large internuclear separations, we need to include at least one higher partial wave in the expansion. These higher partial waves however make little contribution to the TDM as both the mixing coefficients and the dipole overlap integrals are generally small.

The first Π state, labelled $B\,^2\Pi$, is almost pure p character and can be considered as the 2p state. The first excited Σ state is the A state which is dominantly composed from 2s and 2p states. The dipole transition from the B to A state is therefore controlled by the 2s component of the A state. The mixing coefficients for the A state are calculated by retaining only the $l = 0$ and 1 partial waves. It can be seen in figure 2 that our calculated B → A TDM agrees well with that calculated *ab initio* by Theodorakopoulos *et al* (1987). Incidentally if the mixing coefficients for the A state are taken from the

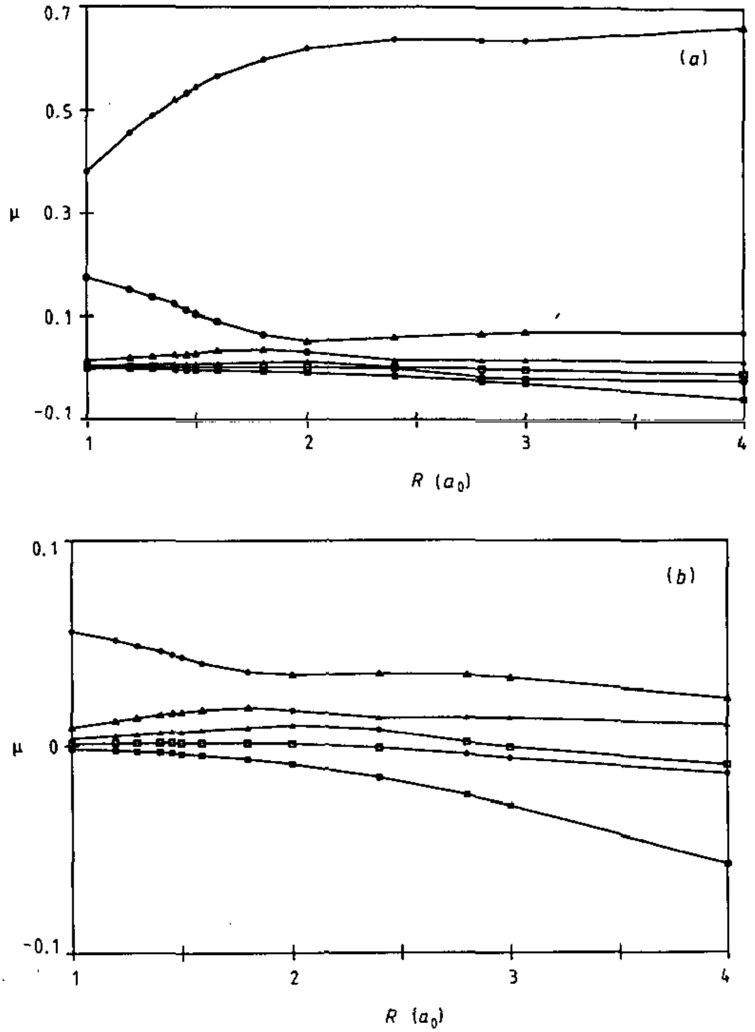

Figure 1. Multichannel quantum defects as a function of R for (a) $^2\Sigma$ and (b) $^2\Pi$ symmetry. The curves indicate the adiabatic states. The symbols denote the dominant l character of each state and therefore correspond to the diabatic picture. Key: ○, s; ●, p; △, d; ▲, f; □, g; ■, h.

scattering calculations where partial waves up to $l = 5$ are retained we observe a dip in the B→A TDM at $R \sim 2a_0$. This feature in the TDM is due to the spurious avoided crossing mentioned above.

When avoided crossings take place the large mixing of different partial waves sometimes results in a change of sign of the phase for one of the dominant partial waves. Although the overall sign of each eigenvector and therefore the sign of the TDM is not significant, the relative sign of each partial wave is significant, resulting in interference between the various 'partial transitions'. This can in some cases result in large and sudden changes in the TDM.

Although some of the fluctuations in the TDM have been explained as being artificial, arising from avoided crossings for higher n states, the sudden fluctuations predicted for D→B and D→A, near $R = 2a_0$, are real features, arising from the interaction

Table 2. Transition dipole moments (in atomic units) of the adiabatic states as a function of *R*. The negative signs in parenthesis indicate arbitrary sign changes of the eigenvector and are to be ignored. The assignments of states are as given by Sarpal *et al* (1991a).

	$^2\Sigma \to {}^2\Sigma$			$^2\Pi \to {}^2\Sigma$		$^2\Sigma \to {}^2\Pi$				$^2\Pi \to {}^2\Pi$	
R	C → A	D → A	F → A	B → A	G → A	I → B	C → B	D → B	F → B	E → B	G → B
1.0	0.67	0.90	1.06	−2.19	−0.93	0.26	−0.92	0.76	−1.10	(−)0.16	1.90
1.2	1.61	0.74	0.89	−2.46	−0.82	0.23	−0.77	0.80	−1.10	(−)0.28	1.89
1.3	1.94	0.67	0.86	−2.55	−0.82	0.18	−0.74	0.83	−1.11	(−)0.36	1.92
1.4	2.21	0.60	0.84	−2.61	−0.83	0.17	−0.70	0.85	−1.11	(−)0.47	1.91
1.455	2.38	0.55	0.83	−2.65	−0.86	0.16	−0.66	0.84	−1.10	(−)0.54	1.90
1.5	2.49	0.51	0.83	−2.68	−0.88	0.16	−0.64	0.85	−1.10	(−)0.61	1.90
1.6	2.71	0.42	0.82	−2.73	−0.96	0.14	−0.58	0.87	−1.08	(−)0.79	1.85
1.8	3.07	0.12	0.81	−2.82	−1.21	0.13	−0.44	1.04	−0.93	(−)1.28	1.60
2.0	3.32	0.46	0.54	−2.89	−1.22	0.13	−0.27	(−)1.37	−0.14	1.76	(−)1.12
2.4	3.41	0.62	−0.11	−2.95	−1.74	0.14	0.14	(−)1.27	0.42	2.12	0.41
2.8	2.99	0.66	−0.47	−2.95	−1.85	0.17	0.51	(−)1.15	0.48	2.20	0.02
3.0	2.65	0.71	−0.62	−2.94	−1.88	0.19	0.65	(−)1.05	0.47	2.21	(−)0.15
4.0	2.46	1.35	−1.00	−3.00	−1.92	(−)0.41	(−)0.86		0.39	2.14	(−)0.77

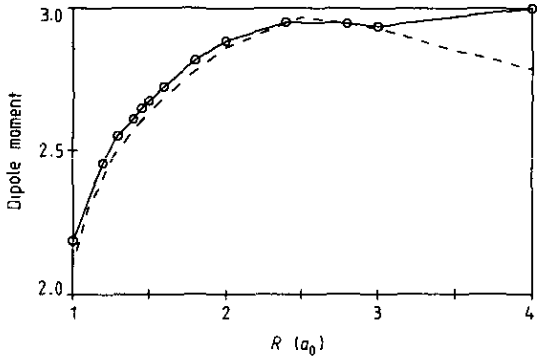

Figure 2. Transition dipole moment for the B → A transition as a function of *R*. The full curve is for our results and the broken curve is due to Petsalakis *et al* (1987).

between the D and F states. However the D → A feature is absent from the calculations of Petsalakis *et al* (1987) (figure 3(*a*)) and the dipole matrix elements presented by van Hemert and Peyerimhoff (1991) but a weaker feature is found in the D → B dipole moment calculated by Petsalakis *et al* (1987).

The transition for which we disagree quite sharply with Petsalakis *et al* (1987) is the E $^2\Pi \to$ B $^2\Pi$ case. Our calculations agree with Petsalakis *et al* for small internuclear separations, where the E state is dominantly of p character. In our calculations we observe a strong interaction between the 3p E $^2\Pi$ and 3d G $^2\Pi$ states at $R \sim 2.0a_0$, with a resultant mixed character for the states. The E state attains a dominant d wave character and the G state p wave character. The TDM of the two adiabatic states are appreciably different from the calculation for E → B made by Petsalakis *et al* (1987) (see figure 3(*b*)). Both the D/F and E/G crossings are found in the calculations of van Hemert and Peyerimhoff (1991). Their crossing between the E and G states is somewhat sharper than ours, suggesting that the interaction between the two states may be overestimated in our calculations.

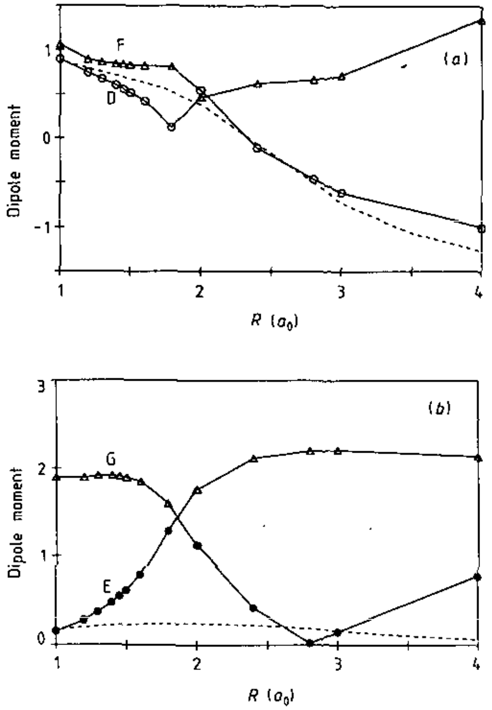

Figure 3. Transition dipoles for (a) D, F → A and (b) E, G → B. Full curves indicate adiabatic upper states and the symbols correspond to diabatic states; broken curves are due to Petsalakis *et al* (1987).

The inability of the previous calculations of TDM to produce the sudden fluctuations found by us can be put down to the higher interacting state not having been included in these calculations. This is easily demonstrated when we expand the D state with $l = 0$ and 1 partial waves only, thereby removing the 3d F $^2\Sigma$ state. We then reproduce the results of Petsalakis *et al* (1987) for the D → A transition quite accurately. A similar result is found for the E → B transition.

Sarpal *et al* (1991a) commented on the closeness in energy of the 3d G $^2\Pi \rightarrow$ 2s A $^2\Sigma$ and 3p I $^2\Sigma \rightarrow$ 2p B $^2\Pi$ transitions, and how this could result in some of the weaker transitions observed. The first transition has a large dipole moment for the whole range of internuclear distances. In the equilibrium separation region the I → B TDM is approximately one fifth of the G → A TDM. This suggests that the I → B may be important in explaining the weaker features found in this energy range.

In conclusion a comparison of our dipole moments with the *ab initio* ones of Petsalakis *et al* (1987) demonstrates the usefulness of this approach to transitions involving highly excited states. Even those transitions involving a state with a large quantum defect are accurately calculated by this method. Our calculations reveal fluctuations in the TDM near curve crossings which have not previously been predicted for HeH. We suggest that our results in these regions will be reproduced by the *ab initio* calculations which include the higher states involved in the avoided crossings.

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