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Variational approximations to the $2p\sigma_u$ and $2p\pi_u$ wavefunctions of the hydrogen molecule ion

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Abstract. It is shown that trial wavefunctions for the $2p\sigma_u$ and $2p\pi_u$ states of H_2^+ with three variational parameters, separable in elliptic coordinates give excellent results for the energy eigenvalues as functions of the internuclear coordinate. It is also seen that there are two minima for the energy as a function of the parameters. Earlier results for the same trial function used for the $2p\sigma_u$ state in error because the optimization has not always been carried out for the absolute minimum.

The trial wavefunction for the ground state of the ion-molecule H_2^+ with three variational parameters, separable in elliptic coordinates has been studied by Bhalla and Khubchandani (1967), and Clark and Stewart (1969), who showed the presence of a double minimum for the energy in the plane of the two parameters α, p belonging to the part of the wavefunction depending on the elliptic ξ coordinate; they were able to improve the energy obtained by using the correct absolute minimum.

Hariharan and Khubchandani (1968) have studied the first excited state of H_2^+ using the trial function

$$\psi_{2p\sigma_u} = (1 + pR\xi) e^{-\alpha R\xi} \sinh(\beta R\eta) \quad (1)$$

their results for α and p show a strong dependence on the internuclear distance R and the energy obtained is a poor approximation to the known exact values at small R . One of the trial functions used by Dalgarno and Poots (1954) for this state was

$$\psi_{2p\sigma_u} = R\xi\eta e^{-\alpha R\xi} \quad (2)$$

which is a particular case, apart from normalization factors, of (1) when $p \rightarrow \infty$ and $\beta \rightarrow 0$; the approximation to the energy obtained from form (2) should not be better than that found from form (1). It can be seen that this rule is not satisfied for $R = 0.8$ and 1.2 Bohrs, and we can expect the presence of more than one extreme for the energy as a function of α and p .

We used the form (1) for the $2p\sigma_u$ state, and we also studied the lowest π state of H_2^+ with three parameter separable function

$$\psi_{2p\pi_u} = (1 + pR\xi) e^{-\alpha R\xi} \cosh(\beta R\eta) \cos \phi. \quad (3)$$

We have found two minima for the energy on the plane α, p for both states; the corresponding values of β are slightly different, they are not equal because the energy is not separable into a function of the parameters α, p and a function of the parameter β .

The energies obtained give a satisfactory agreement with the exact values of Bates *et al* (1953), as can be seen from table 1.

The results of Hariharan and Khubchandani for the $2p\sigma_u$ state correspond to the absolute minimum for $R = 0.4, 3.0$ and 4.0 Bohr, and to the relative one for other values of R .

It can be seen that the energy has five to six correct digits and is better than any of the values obtained with the trial functions used by Dalgarno and Poots and Moiseiwitsch and Stewart (1954) for these states. Even though the energy is not a very

Table 1. Parameters and energy for the variational approximation

R	β	p	α	$-E^\dagger$
The $2p\sigma_u$ state				
0.40	0.391156	9.52978	0.508771	0.510782
				0.51079
0.80	0.404106	2.199955	0.531509	0.542738
				0.54274
1.00	0.412651	1.388457	0.545550	0.564804
				0.564814
1.20	0.421780	0.968764	0.559543	0.588594
				0.58861
1.60	0.439090	0.576714	0.583244	0.633612
				0.63361
2.00	0.452710	0.407067	0.598744	0.667532
				0.667534
2.40	0.462280	0.317878	0.606936	0.688575
				0.68857
3.00	0.470984	0.244878	0.610112	0.701417
				0.701418
4.00	0.477465	0.184594	0.603698	0.695548
				0.695551
The $2p\pi_u$ state				
0.40	0.222635	0.024461	0.516919	0.494965
				0.49496
0.80	0.220193	0.045905	0.520656	0.482194
				0.48219
1.00	0.218661	0.054607	0.518950	0.474104
				0.474108
1.20	0.217022	0.062054	0.515701	0.465389
				0.46539
1.60	0.213624	0.073845	0.506358	0.447106
				0.44711
2.00	0.210276	0.082531	0.495123	0.428769
				0.428772
2.40	0.207119	0.089068	0.483302	0.411088
				0.41109
3.00	0.202865	0.096206	0.465815	0.386442
				0.386444
4.00	0.197164	0.103926	0.439165	0.350823
				0.350825

† The results are given in Hartree atomic units. The last entry of the energy column is the exact value for that internuclear distance, taken from Bates *et al* (1953) for non integer values of R , and from Bates and Reid (1968) for integer R .

sensitive parameter to variations in the form of the wavefunction, we can conclude that the selection of the simplest function separable in elliptic coordinates which can adopt the correct united and separated atoms forms will bring a satisfactory description of the eigenstates of H_2^+ .

The computations were done on the IBM system of the Computer Centre of the Centro Atómico Bariloche.

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