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Approximate Wave Functions for Excited States: Energies and Dipole Moments of the $2p\sigma$ State of HeH^{+2}

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The problem of calculating approximate wave functions for an excited state, which is *not* the lowest of a symmetry species, has been investigated for the first excited σ-state of the HeH^{+2} ion. The results of calculations using explicitly orthogonalized variational trial functions are compared with results based on the linear combination of molecular orbitals (LCMO) procedure, and with the exact values. Our values of the electronic energy and of the dipole moment are in good agreement with the exact values.

Das Problem der Berechnung eines angeregten Zustands, der nicht der niedrigste seiner Rasse ist, wird am Beispiel des ersten angeregten σ-Zustands von HeH^{+2} diskutiert. Energien, Dipolmomente und Übergangsmomente, erhalten mit nichtorthogonalisierten und orthogonalisierten Variationsstörungsfunktionen 0. und 1. Ordnung und mit LCMO-Funktionen, werden mit den exakten Werten verglichen.

On étudie le problème du calcul d'une fonction d'onde approchée pour un état excité qui n'est *pas* le plus bas pour sa classe de symétrie, sur l'exemple du premier état σ excité de l'ion HeH^{+2}. Les résultats du calcul par utilisation de fonctions d'essai variationnelles explicitement orthogonalisées sont comparés à ceux fondés sur un procédé de combinaison linéaire des orbitales moléculaires (LCMO) et aux valeurs exactes. Nos valeurs pour l'énergie électronique et le moment dipolaire sont en bon accord avec les valeurs exactes.

1. Introduction

In some recent work [4, 5, 6 (1, 2, 3)] we have described a variation-perturbation procedure for calculating accurate approximate molecular orbitals for a number of states of H_2^+ and HeH^{+2}. Our procedure consists of two parts. First, we select according to the prescription of DALGARNO and LEWIS [7] a two-centre approximate function $\psi_0(\alpha)$ say, of *united atom* type, which contains an adjustable charge parameter α to be chosen later. This single-parameter function serves as the zero-order (unperturbed) approximation of conventional Rayleigh-Schrödinger perturbation theory, and we calculate the first-order correction $\psi_1(\alpha)$ say, directly. With the zero- and first-order functions $\psi_0(\alpha)$ and $\psi_1(\alpha)$ known, we next construct a two-parameter variational trial function,

$$\psi_t(\alpha, \eta) = \psi_0(\alpha) + \eta\, \psi_1(\alpha) \tag{1}$$

and seek the optimum values of the charge parameter α and the linear parameter η.

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Our previous calculations were concerned with states which are the *lowest* of some symmetry, so that the choice of parameters according to the usual variational criterion has always led to calculated (approximate) energies which are upper bounds on the exact energies of the corresponding states. For *excited* states, the variational procedure requires modification, whereas the choice of $\psi_0(\alpha)$ and the calculation of $\psi_1(\alpha)$ proceeds as before.

2. The $2p\sigma$ State

For the $2p\sigma$ state, we choose the (unnormalized) trial function

$$\Psi_t^1\,(2p\sigma) = \chi_0(\beta) + \chi_1(\beta) \tag{2}$$

where $\chi_0(\beta)$ is the united atom approximation

$$\chi_0(\beta) = \lambda\mu \exp\,(-\beta R\lambda) = \lambda\mu \exp\,(-q\lambda)\,,\ \text{say.} \tag{3}$$

Here, as in our earlier work, the internuclear separation is $2R$ a.u. while λ and μ are the usual confocal elliptic coordinates [4]. The calculation of $\chi_1(\beta)$ now proceeds exactly as for the $2p\sigma_u$ state of H_2^+ [4] and we find

$$\chi_1(\beta) = \chi_0(\beta)\left[a + \frac{b}{\mu} + c\mu + d\mu^2 + \frac{e}{\lambda} + f\lambda + g\ln\lambda + h\ln(\lambda+1)\right]. \tag{4}$$

The coefficient a appearing in Eq. (4) is determined from the normalization condition

$$\langle\chi_1(\beta)\,|\,\chi_0(\beta)\rangle = 0\,, \tag{5}$$

and the remaining coefficients are listed in Table 1. This solution differs from the corresponding solution for the $2p\sigma_u$ state of H_2^+ only in the terms linear in μ, which arise directly from the lack of nuclear symmetry in HeH^{+2}.

Table 1. *Values of the Constants in Eq. (4)*

$$b = \frac{R}{2}$$

$$c = -\frac{R}{2}$$

$$d = \frac{1}{10}\,(q^2 - 2\,E_1\,R^2)$$

$$e = [6\,E_1\,R^2(5 - q^2) + 45\,qR + 2\,q^2(4\,q^2 - 15)]/20\,q^5$$

$$f = E_1\,R^2/q$$

$$g = -2\,qe$$

$$h = [2\,E_1\,R^2(7\,q^2 + 15) + 15\,qR(2\,q^2 + 3) - 6\,q^2(2\,q^2 + 5)]/10\,q^4$$

where $q = \beta R$ and E_1 is the first order energy

3. Orthogonality

The exact wave functions Ψ^0 and Ψ^1 for the $1s\sigma$ and $2p\sigma$ states respectively, satisfy

$$\langle\Psi^0\,|\,\Psi^1\rangle = 0 \tag{6a}$$

and

$$\langle \Psi^0 \mid H \mid \Psi^1 \rangle = 0 \tag{6b}$$

where H is the Hamiltonian of the system. Although the trial function Ψ_t^1 of Eq. (2) for the $2p\sigma$ state and the corresponding trial function, namely

$$\Psi_t^0(1s\sigma) = \psi_0(\alpha) + \eta\, \psi_1(\alpha) \tag{7}$$

for the $1s\sigma$ state [6 (1)] do *not* satisfy these relations, the united atom approximations $\psi_0(\alpha)$ and $\chi_0(\beta)$ are *orthogonal* for *all* values of α and β, but it is easily verified that $\langle \psi_0 \mid H \mid \chi_0 \rangle$ is *not* zero.

4. Energy Calculations with an Unorthogonalized $2p\sigma$ State Wave Function

If $\psi_0(\alpha)$ were a good approximation to the exact ground-state eigenfunction Ψ^0, we should expect reasonable energy values for the $2p\sigma$ state to result from calculations using $\chi_0(\beta)$, with β suitably chosen. Unfortunately, when $\beta = 1.5$ (the united atom value for this state) the calculated energies are much too low over almost the entire range of R-values (see Table 3). This is a reflection of the inaccuracy of $\psi_0(\alpha)$ as a representation of Ψ^0 which has been noted previously [6 (1)].

The inclusion of $\chi_1(\beta)$ (again with $\beta = 1.5$) leads to much more satisfactory energies over most of the range, implying that the approximate wave function including the first-order correction is more nearly orthogonal to the exact ground-state solution Ψ^0. The energies calculated with $\Psi_t^1(\beta = 1.5)$ are presented in Table 3 and are generally in close agreement with the exact values [2, 8] up to $R = 1.75$ even for those few R-values where the approximate energies are still not bounds. For larger R-values, the differences become appreciable, but the accuracy of our approximation for moderate R-values is gratifying, since $\chi_0(\beta)$ is chosen to display the correct behaviour in the limit as $R \to 0$.

Variation of β can only lower the energies still further, and it is therefore clear that we must construct a properly orthogonalized wave function to achieve bounds on the energy.

5. Energy Calculations with Orthogonalized $2p\sigma$ State Wave Functions

5.1 Choice of the Charge Parameters α and β

We have calculated α and β by solving the second order secular equation, which results from variation of the linear parameters in the "zero order" trial wave function

$$\Phi_t = a\psi_0(\alpha) + b\chi_0(\beta)\,. \tag{8}$$

In principle, it is possible to determine *two pairs* of values which separately optimize the energies of the $1s\sigma$ and $2p\sigma$ states. However, we found that one eigenvalue of the secular equation is sensitive only to variations in α and the other eigenvalue is sensitive only to variations in β. The resulting values of α and β are listed in Table 2.

5.2 The $1s\sigma$ State Wave Function

For the lower $1s\sigma$ state, we have calculated energy bounds by optimizing the total energy through third order by varying η in the linear trial function (7). The

Table 2. *Values of the Parameters for the* $1s\sigma$ *and* $2p\sigma$ *States of* HeH^{+2}

R[a]	α	β	η	k_0	k_1	l	m
0.125	2.779	1.534	1.020	5.28 (−1)[b]	1.26 (−2)	2.19 (−5)	7.56 (−3)
0.250	2.527	1.621	1.077	5.23 (−1)	3.15 (−2)	3.00 (−4)	2.29 (−3)
0.375	2.334	1.727	1.150	4.99 (−1)	4.63 (−2)	9.54 (−4)	3.84 (−2)
0.500	2.189	1.810	1.227	4.68 (−1)	5.64 (−2)	1.11 (−3)	5.26 (−2)
0.750	1.989	1.852	1.357	4.19 (−1)	6.88 (−2)	−8.24 (−3)	7.85 (−2)
1.000	1.852	1.791	1.428	3.85 (−1)	7.22 (−2)	−3.51 (−2)	9.78 (−2)
1.250	1.745	1.697	1.439	3.62 (−1)	6.83 (−2)	−6.88 (−2)	1.10 (−1)
1.500	1.656	1.599	1.410	3.48 (−1)	6.03 (−2)	−9.77 (−2)	1.19 (−1)
1.750	1.579	1.508	1.360	3.41 (−1)	5.00 (−2)	−1.17 (−1)	1.27 (−1)
2.000	1.511	1.425	1.300	3.39 (−1)	3.82 (−2)	−1.29 (−1)	1.34 (−1)
2.500	1.395	1.286	1.177	3.46 (−1)	1.07 (−2)	−1.34 (−1)	1.52 (−1)

[a] The internuclear separation is 2 R.

[b] 5.28 (−1) = $5.28 \cdot 10^{-1}$.

resulting values of η are listed in Table 2, and the corresponding energies in Table 3. These energies differ very little from the best values obtained earlier [6 (1)] with slightly different values of α and η, and it is clear that the approximate function Ψ_t^0 is an adequate representation of the exact ground state function Ψ^0 only up to $R = 1.5$.

5.3 *Explicitly Orthogonalized* $2p\sigma$ *State Wave Functions*

The unnormalized function

$$\Phi_t^1 = \Psi_t^1 + k\,\Psi_t^0 \tag{9}$$

where

$$k = -\langle \Psi_t^1 \mid \Psi_t^0 \rangle / \langle \Psi_t^0 \mid \Psi_t^0 \rangle\,, \tag{10}$$

is orthogonal to Ψ_t^0. Here, Ψ_t^0 is given by Eq. (7) and Ψ_t^1 is given either by

$$\Psi_t^1 = \chi_0(\beta)\,, \qquad [\text{with } k = k_0 \text{ in Eq. (9)}] \tag{11a}$$

or by

$$\Psi_t^1 = \chi_0(\beta) + \chi_1(\beta)\,, \quad [\text{with } k = k_1 \text{ in Eq. (9)}]. \tag{11b}$$

The energies calculated with these Φ_t^1 are presented in Table 3. They are all bounded by the exact values, but the zero order values are very inaccurate. Much better accuracy results from the first order calculations, but it is clear that we have obtained upper bounds at the price of a loss of accuracy over most of the range of R-values. The effect of orthogonalization may be seen to be small from the values of the constants k_0 and k_1 (see Table 2), and by comparing the energies calculated with orthogonalized trial functions and with the *corresponding* unorthogonalized trial functions (i.e., with the same values of β). These values are also included in Table 3.

This procedure of explicit orthogonalization towards approximate ground state eigenfunctions was followed in earlier purely variational calculations on the diatomic ions [3, 7, 9].

Table 3. *Total Electronic Energies, $-E$, of the $1s\sigma$ and $2p\sigma$ States of* HeH^{+2} *(in Atomic Units)*

	$1s\sigma$ state			$2p\sigma$ state							
	First-order functions		Exact values	Zero-order functions			First-order functions				Exact values
R	(1)	(2)	(3)	(4)	(5)	(6)	(4)	(5)	(6)	(7)	(3)
0.125	4.13327	4.13327	4.13365	1.14482[a]	1.14569[a]	1.14105	1.14376	1.14377	1.14376	1.14377	1.14378
0.250	3.66333	3.66334	3.66554	1.19388	1.20441[a]	1.18190	1.19735	1.19767	1.19763	1.19762	1.19776
0.375	3.29519	3.29520	3.30137	1.25432	1.28984[a]	1.23178	1.26968	1.27151	1.27116	1.27114	1.27168
0.500	3.01997	3.01998	3.03335	1.31265	1.37949[a]	1.27175	1.33522	1.33847[a]	1.33711	1.33711	1.33834
0.750	2.65350	2.65360	2.69546	1.39784[a]	1.49693[a]	1.28213	1.39018[a]	1.39114[a]	1.38466	1.38456	1.38844
1.000	2.42157	2.42255	2.51219	1.43426[a]	1.51983[a]	1.22365	1.35343[a]	1.35050[a]	1.33739	1.33641	1.34519
1.250	2.25156	2.25443	2.40489	1.43249[a]	1.48786[a]	1.14778	1.27239[a]	1.26837[a]	1.25149	1.24861	1.26455
1.500	2.11254	2.11800	2.33549	1.40611[a]	1.43178[a]	1.07820	1.17941[a]	1.17673	1.15987	1.15442	1.17883
1.750	1.99221	2.00049	2.28680	1.36559[a]	1.36740[a]	1.01932	1.08937	1.08913	1.07487	1.06659	1.09995
2.000	1.88535	1.89639	2.25061	1.31786[a]	1.30215[a]	0.96955	1.00761	1.01004	0.99955	0.08851	1.03108
2.500	1.70239	1.71824	2.20024	1.21628[a]	1.18032[a]	0.88866	0.87154	0.87867	0.87619	0.86034	0.92255

[a] These values are not bounds.

(1) α and η from Table 2.

(2) LCMO functions.

(3) Hunter and Pritchard [8].

(4) Unorthogonalized functions, $\beta = 1.5$.

(5) Unorthogonalized functions, β from Table 2.

(6) *Orthogonalized functions, β from Table 2.*

(7) LCMO functions, β from Table 2.

Table 4. *Dipole Moments and Transition Matrix Elements for the* $1s\sigma$ *and* $2p\sigma$ *States of* HeH^{+2}

R	$1s\sigma$ state dipole moments			$2p\sigma$ state dipole moments				$1s\sigma - 2p\sigma$ dipole transition matrix elements			
	(1)	(2)	(3)	(1)	(4)	(2)	(5)	(1)	(4)	(2)	(6)
0.125	0.079	0.079	—	0.206	0.206	0.207	—	0.294	0.293	0.294	0.289
0.250	0.143	0.144	0.137	0.402	0.398	0.406	0.408	0.375	0.374	0.376	0.360
0.375	0.191	0.194	—	0.587	0.572	0.599	—	0.459	0.456	0.463	—
0.500	0.226	0.228	0.180	0.765	0.733	0.796	0.819	0.530	0.523	0.538	0.474
0.750	0.263	0.252	—	1.118	1.044	1.213	—	0.628	0.612	0.637	0.482
1.000	0.275	0.234	0.088	1.460	1.356	1.629	1.675	0.684	0.663	0.793	0.417
1.500	0.282	0.179	0.035	2.071	1.971	2.302	2.491	0.731	0.712	0.603	0.263
2.000	0.320	0.182	0.018	2.602	2.689	2.811	3.343	0.743	0.748	0.482	0.168

(1) Unorthogonalized functions.
(2) LCMO functions.
(3) Exact values (Moiseiwitsch and Stewart [10]).
(4) Orthogonalized functions.
(5) Exact values (McCarroll and Moiseiwitsch [9]).
(6) Exact values (Arthurs et al. [1]).

5.4 Linear Combination Wave Functions

The unnormalized linear combinations of molecular orbitals (LCMO)

$$\Phi_t^0 = \Psi_t^0 + l\,\Psi_t^1 \tag{12}$$

and

$$\Phi_t^1 = \Psi_t^1 + m\,\Psi_t^0 \tag{13}$$

determined from solutions of a secular equation, are orthogonal for all values of α and β.

Values of l and m are presented in Table 2, and their small magnitudes indicate that Φ_t^0 is dominated by Ψ_t^0 and Φ_t^1 by Ψ_t^1. The effect of the mixing is, as usual, to lower the $1s\sigma$ energies and to raise the $2p\sigma$ energies. These energies are presented in Table 3.

Judging by the energy criterion alone, Φ_t^0 is a slightly more accurate representation of the ground-state wave function than Ψ_t^0, whereas the LCMO function Φ_t^1 is apparently less reliable than the explicitly orthogonalized Φ_t^1 of Eq. (9). It should be noted, however, that the energy differences between these approximations are generally much smaller than the discrepancies with the exact values. The most accurate energy values are actually obtained with the *unorthogonalized* Ψ_t^1, but they are not all bounds.

6. Other Molecular Properties: Accuracy of the Wave Functions

The accuracy of the various approximate functions and the effects of orthogonalization have been investigated further by calculating dipole moments for both $1s\sigma$ and $2p\sigma$ states, and transition matrix elements for the $1s\sigma - 2p\sigma$ dipole transition. The calculated values are presented in Table 4 together with values calculated using the exact wave functions [1, 9, 10].

The accuracy of our values of the dipole moments for the $2p\sigma$ state provides some indication of the quality of the approximate solutions for this state, but it is clear that none of the $1s\sigma$ solutions is satisfactory except at very small R-values. We wish to emphasize that the most accurate dipole moments were calculated with the LCMO functions and that the unorthogonalized functions give slightly better results than the explicitly orthogonalized wave functions. This is in marked contrast with the energy calculations described above, and serves to underline once more the inadequency of the energy criterion as the *sole* test of the accuracy of an approximate wave function.

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References

1. ARTHURS, A. M., R. A. B. BOND, and J. HYSLOP: Proc. physic. Soc. (London) **A70**, 617 (1957).
2. BATES, D. R., and T. R. CARSON: Proc. Roy. Soc. **A234**, 207 (1956).
3. CARSON, T. R., and A. DALGARNO: Proc. physic. Soc. (London) **A68** 569, (1955).

4. Cohen, M., and R. P. McEachran: Can. J. Physics **44**, 2809 (1966).
5. —, B. H. Dorrell, and R. P. McEachran: Can. J. Physics **44**, 2827 (1966).
6. —, R. P. McEachran, and S. D. McPhee: (1) Can. J. Physics **45**, 2231 (1967).
—, —, — (2) Can. J. Physics **45**, 2533 (1967).
—, —, — (3) Can. J. Physics **45**, 2749 (1967).
7. Dalgarno, A. and J. T. Lewis: Proc. physic. Soc. (London) **A69**, 285 (1956).
8. Hunter, G., and H. O. Pritchard: J. chem. Physics **46**, 2146 (1967).
9. McCarroll, R., and B. L. Moiseiwitsch: Proc. physic. Soc. (London) **A70**, 507 (1957).
10. Moiseiwitsch, B. L., and A. L. Stewart: Proc. physic. Soc. (London) **A69**, 480 (1956).

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