Proc. Camb. Phil. Soc. (1965), **61**, 207
Printed in Great Britain

H_2^+ wave functions

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(*Received* 9 *July* 1964)

Cohen and Coulson (4) and Cohen (5) have obtained wave-functions and energy levels for the hydrogen molecular ion in a spherical polar representation. They expanded the wave-function in terms of spherical harmonics, and their expansion may be written as

$$\psi(r,\theta,\phi) = \frac{1}{\sqrt{\pi}} \sum_k f_S(r)\, P_S^m(\cos\theta) \cos(m\phi), \tag{1}$$

where $S = 2k$ for even states, and $S = 2k+1$ for odd states.

The coupled differential equations for the radial functions were solved by a digital computer for the case in which the internuclear distance was 2 atomic units. The results, which were presented in numerical form, are in close agreement with the exact (two-centre) results of Bates, Ledsham and Stewart (1). Only the first few radial functions are important.

Analytic fits have been found for the radial functions of some of the lower states, and since they may be of interest they are recorded here. For each state fits have been obtained for the first two radial functions. The method of fitting was inwards, and difficulty was experienced in fitting accurately in the region between the nuclei due to the discontinuity in $d\psi/dr$ at the nuclei.

State $1s\sigma$

$$\psi = \frac{1}{\sqrt{\pi}}[f_0(r)\, P_0(\cos\theta) + f_2(r)\, P_2(\cos\theta)],$$

$$f_0(r) = r \sum_{i=1}^{4} A_i \exp(-\alpha_i r) + A_5 \exp(-\alpha_5 r),$$

$$f_2(r) = r^3 \sum_{i=1}^{4} B_i \exp(-\beta_i r) + B_5 r^2 \exp(-\beta_5 r),$$

$A_1 = +1{\cdot}08417$	$\alpha_1 = 1{\cdot}56598$	$B_1 = +0{\cdot}065719$	$\beta_1 = 1{\cdot}88143$
$A_2 = +1{\cdot}58651$	$\alpha_2 = 2{\cdot}18188$	$B_2 = +1{\cdot}28555$	$\beta_2 = 2{\cdot}77167$
$A_3 = -3{\cdot}07731$	$\alpha_3 = 4{\cdot}96466$	$B_3 = +14{\cdot}2814$	$\beta_3 = 4{\cdot}59120$
$A_4 = +3{\cdot}15557$	$\alpha_4 = 6{\cdot}05640$	$B_4 = -25{\cdot}2532$	$\beta_4 = 6{\cdot}25266$
$A_5 = +0{\cdot}56025$	$\alpha_5 = 4{\cdot}40000$	$B_5 = +0{\cdot}55122$	$\beta_5 = 4{\cdot}39987$

https://doi.org/10.1017/S0305004100038792 Published online by Cambridge University Press

State $2s\sigma$

$$\psi = \frac{1}{\sqrt{\pi}}[f_0(r)\,P_0(\cos\theta) + f_2(r)\,P_2(\cos\theta)],$$

$$f_0(r) = r\sum_{i=1}^{4} A_i \exp(-\alpha_i r), \quad f_2(r) = r^3 \sum_{i=1}^{4} B_i \exp(-\beta_i r),$$

$A_1 = -0{\cdot}906496$	$\alpha_1 = 0{\cdot}822737$	$B_1 = -0{\cdot}0017063$	$\beta_1 = 0{\cdot}927575$
$A_2 = +1{\cdot}05971$	$\alpha_2 = 1{\cdot}04995$	$B_2 = -0{\cdot}010161$	$\beta_2 = 1{\cdot}19086$
$A_3 = +0{\cdot}741545$	$\alpha_3 = 1{\cdot}66742$	$B_3 = +0{\cdot}362350$	$\beta_3 = 2{\cdot}59103$
$A_4 = +0{\cdot}451893$	$\alpha_4 = 2{\cdot}75359$	$B_4 = +3{\cdot}49088$	$\beta_4 = 4{\cdot}13236$

State $2p\sigma$

$$\psi = \frac{1}{\sqrt{\pi}}[f_1(r)\,P_1(\cos\theta) + f_3(r)\,P_3(\cos\theta)],$$

$$f_1(r) = r^2 \sum_{1}^{4} A_i \exp(-\alpha_i r) + rA_5 \exp(-\alpha_5 r),$$

$$f_3(r) = r^4 \sum_{1}^{4} B_i \exp(-\beta_i r) + r^3 B_5 \exp(-\beta_5 r),$$

$A_1 = +0{\cdot}32067$	$\alpha_1 = 1{\cdot}2852$	$B_1 = +0{\cdot}02855$	$\beta_1 = 1{\cdot}8690$
$A_2 = +1{\cdot}2945$	$\alpha_2 = 1{\cdot}7872$	$B_2 = +0{\cdot}91773$	$\beta_2 = 3{\cdot}0585$
$A_3 = +3{\cdot}4332$	$\alpha_3 = 2{\cdot}8511$	$B_3 = +15{\cdot}102$	$\beta_3 = 5{\cdot}0890$
$A_4 = -8{\cdot}7639$	$\alpha_4 = 6{\cdot}4000$	$B_4 = -162{\cdot}86$	$\beta_4 = 9{\cdot}4000$
$A_5 = +3{\cdot}3230$	$\alpha_5 = 8{\cdot}5000$	$B_5 = +43{\cdot}820$	$\beta_5 = 10{\cdot}000$

State $2p\pi$

$$\psi = \frac{1}{\sqrt{\pi}}[f_1(r)\,P_1^1(\cos\theta) + f_3(r)\,P_3^1(\cos\theta)]\cos\phi,$$

$$f_1(r) = r^2 \sum_{i=1}^{3} A_i \exp(-\alpha_i r) + rA_4 \exp(-\alpha_4 r),$$

$$f_3(r) = r^4 \sum_{i=1}^{3} B_i \exp(-\beta_i r),$$

$A_1 = +0{\cdot}229062$	$\alpha_1 = 1{\cdot}00169$	$B_1 = +0{\cdot}0007682$	$\beta_1 = 1{\cdot}30167$
$A_2 = +0{\cdot}511548$	$\alpha_2 = 1{\cdot}45927$	$B_2 = +0{\cdot}018063$	$\beta_2 = 2{\cdot}05629$
$A_3 = +0{\cdot}361353$	$\alpha_3 = 2{\cdot}70000$	$B_3 = +0{\cdot}189457$	$\beta_3 = 3{\cdot}43299$
$A_4 = +0{\cdot}332165$	$\alpha_4 = 3{\cdot}00000$		

State $3d\pi$

$$\psi = \frac{1}{\sqrt{\pi}}[f_2(r)\,P_2^1(\cos\theta) + f_4(r)\,P_4^1(\cos\theta)]\cos\phi,$$

$$f_2(r) = r^3 \sum_{i=1}^{4} A_i \exp(-\alpha_i r), \quad f_4(r) = r^5 \sum_{i=1}^{3} B_i \exp(-\beta_i r)$$

$A_1 = +0{\cdot}0082978$	$\alpha_1 = 0{\cdot}72296$	$B_1 = +0{\cdot}00003575$	$\beta_1 = 1{\cdot}06918$
$A_2 = +0{\cdot}0235932$	$\alpha_2 = 0{\cdot}94700$	$B_2 = +0{\cdot}0011036$	$\beta_2 = 1{\cdot}78095$
$A_3 = +0{\cdot}0533682$	$\alpha_3 = 1{\cdot}44636$	$B_3 = +0{\cdot}024554$	$\beta_3 = 3{\cdot}16177$
$A_4 = +0{\cdot}118523$	$\alpha_4 = 2{\cdot}54775$		

https://doi.org/10.1017/S0305004100038792 Published online by Cambridge University Press

Values of $\bar{X}^2$, $\bar{Z}^2$ and dipole length transition integrals have been calculated using these fitted functions, and are given in Tables 1 and 2, together with the exact values, and the values given by Cohen. The exact values are given in, or can be deduced from, references (2), (3), (6), and (7), and were calculated using the exact wave functions of Bates, Ledsham and Stewart. The values given by Cohen were calculated using three radial functions.

Table 1

	Fitted		Exact		Cohen	
State	$\bar{X}^2$	$\bar{Z}^2$	$\bar{X}^2$	$\bar{Z}^2$	$\bar{X}^2$	$\bar{Z}^2$
$1s\sigma$	0·641	1·101	$0·64_2$	$1·11_1$	0·646	1·111
$2s\sigma$	$6·34_5$	7·23	—	—	—	—
$2p\sigma$	0·846	3·163	$0·83_6$	$3·14_7$	0·842	3·161
$2p\pi$	6·10	2·28	$6·1_0$	$2·2_8$	—	—
$3d\pi$	12·72	13·22	$12·7_1$	$13·2_3$	—	—

Table 2

$Q_L = |\int \psi_f^* r \psi_i d\tau|$

Transition	Fitted	Exact	Cohen
$1s\sigma \rightarrow 2p\sigma$	1·052	$1·04_9$	1·050
$1s\sigma \rightarrow 2p\pi$	0·717	$0·71_6$	—
$2p\sigma \rightarrow 2s\sigma$	0·827	0·82	—
$2p\pi \rightarrow 2s\sigma$	1·659	1·67	—
$2p\sigma \rightarrow 3d\pi$	0·683	$0·67_5$	—
$2p\pi \rightarrow 3d\pi$	1·437	1·43	—

The results indicate that even for σ states, fitting just the first two radial functions gives acceptable wave-functions.

It should be noted that although the $2s\sigma$ state is fitted well for $r > 0·5$, as $r \rightarrow 0$, the fitted value tends to zero, rather than to a constant (0·15). If greater accuracy is required close to the origin, a term $1/\sqrt{\pi} \times 0·264 \exp(-10r)$ should be added, and the function renormalized.

I am indebted to Professor D. R. Bates for suggesting this problem and for constant encouragement, and to Dr M. Cohen for helpful discussions and full access to his numerical work.

The research reported has been sponsored by the U.S. Office of Naval Research for the Research Projects Agency Department of Defense under Contract N 62558-3634.

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https://doi.org/10.1017/S0305004100038792 Published online by Cambridge University Press