CLM-P58

United Kingdom Atomic Energy Authority

RESEARCH GROUP

Preprint

THE ELECTRON ENERGY FOR H_2^+ IN THE GROUND STATE

H. WIND

Culham Laboratory,

Culham, Abingdon, Berkshire

1964

UNCLASSIFIED
Approved for publication)

CLM - P 58

THE ELECTRON ENERGY FOR H_2^+ IN THE GROUND STATE

by

H. Wind

(Submitted for publication in Journal of Chemical Physics)

A B S T R A C T

The $1s\sigma_g$ state of the hydrogen molecular ion is investigated. The result is given as a table in which the electronic energy for a two Coulomb-centre is given in 7 decimal places for values of internuclear separation R up to 20 in steps of 0.05 atomic units.

* On leave from F.O.M. Instituut voor Plasma Fysica, Rijnhuizen, Jutphaas, Nederland.

U.K.A.E.A. Research Group,
Culham Laboratory,
Nr. Abingdon,
Berks.

August 1964 (C/18 MEA)

The field dissociation H_2^+ is an important process for the injection of protons into mirror machines[1-2]. The probability of field dissociation depends on the energy of the uppermost vibrational levels. To calculate these energy levels it is necessary[3] to have an accurate value for the electronic energy as a function of the internuclear separation R.

As shown originally by Burrau[4], the Schrodinger equation for a two Coulomb-centre can be separated, and the electronic energy E thus calculated exactly. Bates, et al[5] have calculated this energy for values of R up to 9 (atomic units are used throughout this paper), but this is not enough to determine the energies of the highest levels. Cohen et al[6], using a variational method, calculated the energy up to R = 20. However, this result is not sufficiently accurate for our purpose. We have therefore calculated the electronic energy for the ground state $1s\sigma_g$ up to R = 40 in 7 exact decimal places.

The Schrödinger equation, expressed in confocal elliptic coordinates, λ and μ, and an azimuthal angle ϕ is, in atomic units,

$$\frac{\partial}{\partial\lambda}\left\{(\lambda^2-1)\frac{\partial\psi}{\partial\lambda}\right\}+\frac{\partial}{\partial\mu}\left\{(1-\mu^2)\frac{\partial\psi}{\partial\mu}\right\}+\left\{\frac{1}{\lambda^2-1}+\frac{1}{1-\mu^2}\right\}\frac{\partial^2\psi}{\partial\phi^2}$$

$$+\left\{\tfrac{1}{2}R^2E(\lambda^2-\mu^2)+2R\lambda\right\}\psi=0$$

Writing

$$\psi(\lambda,\mu,\phi)=\Lambda(\lambda)\,M(\mu)\,\Phi(\phi).$$

and $p^2=-\frac{1}{2}R^2E$,

the following equations are obtained ,

$$\frac{d^2\Phi}{d\phi^2} = - m^2 \Phi \qquad \ldots (1)$$

$$\frac{d}{d\mu}\left\{(1 - \mu^2)\frac{dM}{d\mu}\right\} + \left\{- A + p^2\mu^2 - \frac{m^2}{1 - \mu^2}\right\} M = 0 \qquad \ldots (2)$$

$$\frac{d}{d\lambda}\left\{(\lambda^2 - 1)\frac{d\Lambda}{d\lambda}\right\} + \left\{A + 2R\lambda - p^2\lambda^2 - \frac{m^2}{\lambda^2 - 1}\right\} \Lambda = 0 \qquad \ldots (3)$$

where A is the separation constant. We will restrict ourselves to the case m = o, since we will calculate the electronic energy for the ground state $1s\sigma_g$.

(1) Gives immediately $\Phi(\phi) = e^{im\phi} = 1$.

To solve (2) we have followed the method of Hylleraas[7], writing

$$M(\mu) = \sum_{\ell=o}^{\infty} c_\ell P_\ell(\mu)$$

$P_\ell(\mu)$ being Legendre functions. When using the recurrence relation

$$(1 - \mu^2) P_n''(\mu) - 2\mu P_n'(\mu) + n(n + 1) P_n(\mu) = 0$$

(2) gives a recurrence relation for c_ℓ*

$$\frac{(\ell - 1)\ell}{(2\ell - 3)(2\ell - 1)} p^2 c_{\ell - 2}$$

$$+ \left\{- A - \ell(\ell + 1) + \left[\frac{(\ell + 1)^2}{(2\ell + 3)(2\ell + 1)} + \frac{\ell^2}{(2\ell + 1)(2\ell - 1)}\right] p^2\right\} c_\ell$$

$$+ \frac{(\ell + 2)(\ell + 1)}{(2\ell + 5)(2\ell + 3)} p^2 c_{\ell+2} = 0 .$$

---

* There appears to be a misprint in the original paper by Hylleraas. In equation (9c) a factor C has been omitted in the last term on the left hand side.

This recurrence relation is considered as an infinite set of homogeneous linear equations, in which the determinant of the coefficient matrix must be zero. This determinant contains p and A and, by equating it to zero, A is defined as a function of p. For the ground state ℓ is even, for ℓ odd we would find the solution for the $2p\sigma_u$ state. Since this determinant has an infinite number of terms it is difficult to be certain of the number of terms which must be taken into account in order to achieve the required accuracy. However only diagonal and neighbouring terms exist and in view of the simplicity and speed of calculating such a determinant by computer, we have considered a 50 × 50 determinant (notation D (50)). Taking into account only D (10) does in fact lead to exactly the same values of A as a function of p in 9 decimal places.

Having calculated A as a function of p, we substitute these values in (3) and now calculate E as a function of p, or since $p^2 = -\frac{1}{2} R^2 E$, E as a function of R. We follow the method given by Jaffe[8], putting

$$\Lambda(\lambda) = (\lambda + 1)^{\sigma} y \left(\frac{\lambda - 1}{\lambda + 1}\right) e^{-p\lambda}$$

in which

$$\sigma = \frac{R}{p} - 1$$

and taking

$$y = \ell^{\sum_{0}^{\infty}} g_t \left(\frac{\lambda - 1}{\lambda + 1}\right)^t .$$

Then from (3) the following recurrence relation is found

$$(t - 1 - \sigma)^2 g_{t-1}$$
$$- \{2t + (4p - 2\sigma)t - A + p^2 - (2p + 1)\sigma\} g_t$$
$$+ (t + 1)^2 g_{t+1} = 0 .$$

We now consider this again as a coefficient matrix, the determinant

of which must be zero. We have again taken D (50) into account although D (10) produces the same values of R. In either determinant, both that related to (2) and that related to (3), A and R respectively were adjusted until D (50) changed its sign when A and R changed by less than 10^{-9}.

Some 950 pairs of values for E and R were calculated. E was then calculated for values of R from 0.05 to 39.95 in steps of 0.05 by interpolation. To do so 8 neighbouring values of R for which E had been calculated were taken into account using 4 on each side. Through these 8 points a 7th power polynominal was fitted, and this was then used to calculate E for the specified value of R. To check the accuracy interpolations using 6, 10 and 12 points were also made for all the values of R. The differences between the values obtained using 6, 8, 10 or 12 points were in no case larger than 10^{-7}. The results for R up to 20 are presented in the table.

For small values of R the system can be considered as a perturbed He^+ ion. Bethe[9] has calculated that in this case the energy varies like $-2 + \frac{8}{3} R^2$. We have calculated the energy for some 500 values of $R < 0.05$. Figure 1a shows the accuracy of this approximation.

For larger R the H_2^+ ion consists essentially of a hydrogen atom in the ground-state (energy 0.5) and a separated proton. Since the field produced by the proton is $F = \frac{1}{R^2}$, the energy due to the Stark shift of the ground state of the atom is $-\frac{9}{4R^4}$. The energy of the two protons is $+\frac{1}{R}$, so that the electron energy for large R will approach

$$-0.5 - \frac{1}{R} - \frac{9}{4R^4} .$$

Figure 1b shows the accuracy of this approximation.

In the table given by Cohen et al[3], the energy varies more like $-0.5 - \frac{1}{R} - \frac{2}{R^4}$ for large R. This may be due to the method of approximation used in their calculations.

The author is grateful to Dr. J.R. Hiskes and to Dr. A.C. Riviere for their suggestions and valuable discussions.

REFERENCES

1. H. Postma, G.R. Haste, and J.L. Dunlap. Nuclear Fusion 3, 128 (1963)

2. J.R. Hiskes. Phys. Rev. 122, 1207 (1961)

3. S. Cohen, J.R. Hiskes, and R.J. Riddell. Phys. Rev. 119, 1025 (1960)

4. Ø. Burrau. Kgl. Danske, Vid. Selsk. 7, No.14 (1927)

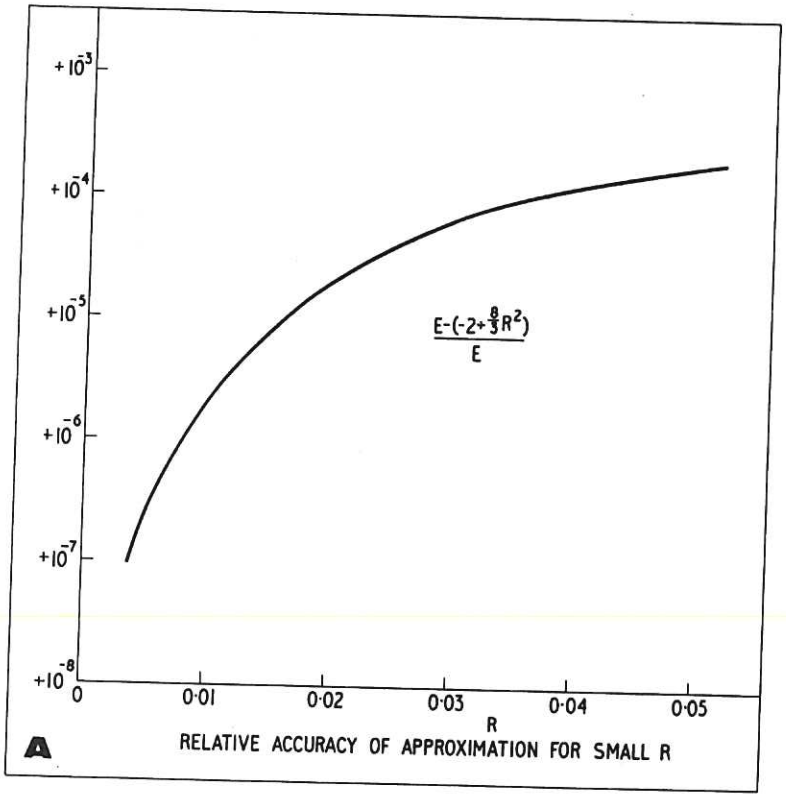
5. D.R. Bates, K. Ledsham, and A.L. Stewart. Phil. Trans. Roy. Soc. London, Ser. A, 246, 215 (1954)

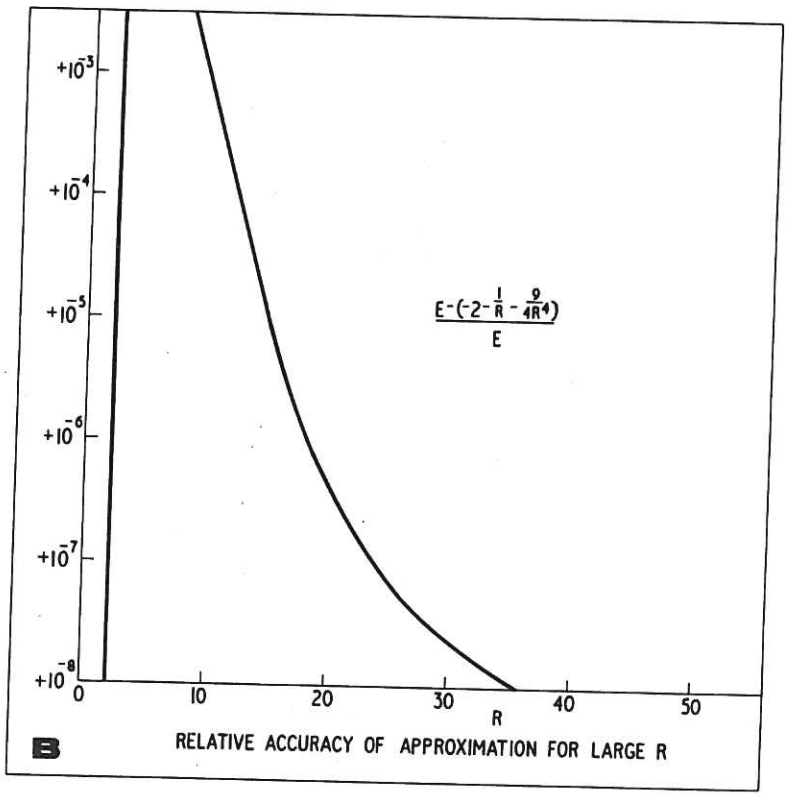
6. S. Cohen, D.L. Judd, and R.J. Riddell. University of California, Lawrence Radiation Laboratory, Rept. No.UCRL-8802 (June, 1959)

7. E.A. Hylleraas, Z. Phys. 71, 739 (1931)

8. G. Jaffe. Z. Phys. 87, 535, (1934)

9. H. Bethe. Quantenmechanik der Ein- und Zwei- Elektronenprobleme, p.527. In Handbuch der Physik, ed. by H. Geiger and K. Scheel, 24/1, Springer-Verlag, 1933.





CLM-P 58 Fig. 1

The results of the calculation are compared with results obtained from two approximations, (a) for small and (b) for large values of R. It can be seen that in both cases the approximations become exact

Table 1. The electronic energy E for the hydrogen molecular ion as a function of the internuclear separation R. Atomic units are used.

R	E	R	E	R	E	R	E
0.05	-1.9939765	5.05	-0.7216226	10.05	-0.6000615	15.05	-0.5664934
0.10	-1.9782421	5.10	-0.7188866	10.10	-0.5995499	15.10	-0.5662726
0.15	-1.9557214	5.15	-0.7162110	10.15	-0.5990439	15.15	-0.5660533
0.20	-1.9286202	5.20	-0.7135943	10.20	-0.5985434	15.20	-0.5658354
0.25	-1.8985570	5.25	-0.7110348	10.25	-0.5980483	15.25	-0.5656190
0.30	-1.8667039	5.30	-0.7085314	10.30	-0.5975584	15.30	-0.5654041
0.35	-1.8339027	5.35	-0.7060825	10.35	-0.5970738	15.35	-0.5651905
0.40	-1.8007539	5.40	-0.7036868	10.40	-0.5965943	15.40	-0.5649783
0.45	-1.7676828	5.45	-0.7013429	10.45	-0.5961198	15.45	-0.5647675
0.50	-1.7349879	5.50	-0.6990497	10.50	-0.5956503	15.50	-0.5645581
0.55	-1.7028754	5.55	-0.6968058	10.55	-0.5951855	15.55	-0.5643501
0.60	-1.6714846	5.60	-0.6946100	10.60	-0.5947256	15.60	-0.5641433
0.65	-1.6409064	5.65	-0.6924610	10.65	-0.5942703	15.65	-0.5639379
0.70	-1.6111962	5.70	-0.6903578	10.70	-0.5938197	15.70	-0.5637339
0.75	-1.5823837	5.75	-0.6882991	10.75	-0.5933735	15.75	-0.5635311
0.80	-1.5544801	5.80	-0.6862839	10.80	-0.5929319	15.80	-0.5633296
0.85	-1.5274832	5.85	-0.6843110	10.85	-0.5924946	15.85	-0.5631294
0.90	-1.5013815	5.90	-0.6823793	10.90	-0.5920616	15.90	-0.5629305
0.95	-1.4761568	5.95	-0.6804879	10.95	-0.5916329	15.95	-0.5627328
1.00	-1.4517863	6.00	-0.6786357	11.00	-0.5912083	16.00	-0.5625364
1.05	-1.4282441	6.05	-0.6768217	11.05	-0.5907879	16.05	-0.5623412
1.10	-1.4055027	6.10	-0.6750449	11.10	-0.5903715	16.10	-0.5621472
1.15	-1.3835336	6.15	-0.6733044	11.15	-0.5899590	16.15	-0.5619544
1.20	-1.3623078	6.20	-0.6715993	11.20	-0.5895505	16.20	-0.5617628
1.25	-1.3417965	6.25	-0.6699286	11.25	-0.5891459	16.25	-0.5615724
1.30	-1.3219714	6.30	-0.6682914	11.30	-0.5887450	16.30	-0.5613832
1.35	-1.3028046	6.35	-0.6666870	11.35	-0.5883479	16.35	-0.5611951
1.40	-1.2842692	6.40	-0.6651144	11.40	-0.5879545	16.40	-0.5610082
1.45	-1.2663393	6.45	-0.6635729	11.45	-0.5875647	16.45	-0.5608225
1.50	-1.2489899	6.50	-0.6620616	11.50	-0.5871784	16.50	-0.5606378
1.55	-1.2321968	6.55	-0.6605798	11.55	-0.5867957	16.55	-0.5604543
1.60	-1.2159372	6.60	-0.6591268	11.60	-0.5864165	16.60	-0.5602719
1.65	-1.2001891	6.65	-0.6577016	11.65	-0.5860407	16.65	-0.5600906
1.70	-1.1849316	6.70	-0.6563038	11.70	-0.5856682	16.70	-0.5599104
1.75	-1.1701446	6.75	-0.6549325	11.75	-0.5852991	16.75	-0.5597313
1.80	-1.1558092	6.80	-0.6535871	11.80	-0.5849332	16.80	-0.5595532
1.85	-1.1419072	6.85	-0.6522669	11.85	-0.5845706	16.85	-0.5593762
1.90	-1.1284216	6.90	-0.6509712	11.90	-0.5842112	16.90	-0.5592002
1.95	-1.1153358	6.95	-0.6496995	11.95	-0.5838549	16.95	-0.5590253
2.00	-1.1026342	7.00	-0.6484511	12.00	-0.5835016	17.00	-0.5588515
2.05	-1.0903021	7.05	-0.6472255	12.05	-0.5831515	17.05	-0.5586786
2.10	-1.0783254	7.10	-0.6460220	12.10	-0.5828043	17.10	-0.5585068
2.15	-1.0666907	7.15	-0.6448400	12.15	-0.5824601	17.15	-0.5583359
2.20	-1.0553851	7.20	-0.6436791	12.20	-0.5821189	17.20	-0.5581661
2.25	-1.0443965	7.25	-0.6425387	12.25	-0.5817805	17.25	-0.5579973
2.30	-1.0337135	7.30	-0.6414182	12.30	-0.5814449	17.30	-0.5578294
2.35	-1.0233249	7.35	-0.6403173	12.35	-0.5811122	17.35	-0.5576625
2.40	-1.0132203	7.40	-0.6392353	12.40	-0.5807823	17.40	-0.5574966
2.45	-1.0033897	7.45	-0.6381718	12.45	-0.5804551	17.45	-0.5573316
2.50	-0.9938235	7.50	-0.6371263	12.50	-0.5801306	17.50	-0.5571676
2.55	-0.9845127	7.55	-0.6360984	12.55	-0.5798087	17.55	-0.5570045
2.60	-0.9754486	7.60	-0.6350877	12.60	-0.5794895	17.60	-0.5568423
2.65	-0.9666229	7.65	-0.6340937	12.65	-0.5791729	17.65	-0.5566811
2.70	-0.9580277	7.70	-0.6331160	12.70	-0.5788588	17.70	-0.5565207
2.75	-0.9496554	7.75	-0.6321542	12.75	-0.5785473	17.75	-0.5563613
2.80	-0.9414989	7.80	-0.6312079	12.80	-0.5782383	17.80	-0.5562028
2.85	-0.9335511	7.85	-0.6302767	12.85	-0.5779317	17.85	-0.5560452
2.90	-0.9258056	7.90	-0.6293603	12.90	-0.5776276	17.90	-0.5558884
2.95	-0.9182560	7.95	-0.6284583	12.95	-0.5773259	17.95	-0.5557325
3.00	-0.9108962	8.00	-0.6275704	13.00	-0.5770266	18.00	-0.5555775
3.05	-0.9037204	8.05	-0.6266962	13.05	-0.5767296	18.05	-0.5554234
3.10	-0.8967231	8.10	-0.6258353	13.10	-0.5764349	18.10	-0.5552701
3.15	-0.8898988	8.15	-0.6249876	13.15	-0.5761425	18.15	-0.5551176
3.20	-0.8832426	8.20	-0.6241526	13.20	-0.5758524	18.20	-0.5549660
3.25	-0.8767494	8.25	-0.6233300	13.25	-0.5755646	18.25	-0.5548153
3.30	-0.8704145	8.30	-0.6225197	13.30	-0.5752789	18.30	-0.5546653
3.35	-0.8642334	8.35	-0.6217212	13.35	-0.5749954	18.35	-0.5545162
3.40	-0.8582017	8.40	-0.6209343	13.40	-0.5747141	18.40	-0.5543679
3.45	-0.8523152	8.45	-0.6201587	13.45	-0.5744349	18.45	-0.5542204
3.50	-0.8465698	8.50	-0.6193942	13.50	-0.5741578	18.50	-0.5540737
3.55	-0.8409617	8.55	-0.6186406	13.55	-0.5738828	18.55	-0.5539277
3.60	-0.8354871	8.60	-0.6178975	13.60	-0.5736098	18.60	-0.5537826
3.65	-0.8301423	8.65	-0.6171648	13.65	-0.5733389	18.65	-0.5536383
3.70	-0.8249238	8.70	-0.6164422	13.70	-0.5730700	18.70	-0.5534947
3.75	-0.8198284	8.75	-0.6157294	13.75	-0.5728031	18.75	-0.5533519
3.80	-0.8148526	8.80	-0.6150264	13.80	-0.5725381	18.80	-0.5532098
3.85	-0.8099934	8.85	-0.6143327	13.85	-0.5722751	18.85	-0.5530685
3.90	-0.8052476	8.90	-0.6136484	13.90	-0.5720140	18.90	-0.5529280
3.95	-0.8006124	8.95	-0.6129730	13.95	-0.5717548	18.95	-0.5527882
4.00	-0.7960849	9.00	-0.6123066	14.00	-0.5714975	19.00	-0.5526492
4.05	-0.7916623	9.05	-0.6116487	14.05	-0.5712421	19.05	-0.5525108
4.10	-0.7873419	9.10	-0.6109994	14.10	-0.5709884	19.10	-0.5523732
4.15	-0.7831211	9.15	-0.6103584	14.15	-0.5707366	19.15	-0.5522363
4.20	-0.7789974	9.20	-0.6097254	14.20	-0.5704866	19.20	-0.5521002
4.25	-0.7749684	9.25	-0.6091005	14.25	-0.5702384	19.25	-0.5519647
4.30	-0.7710317	9.30	-0.6084833	14.30	-0.5699919	19.30	-0.5518300
4.35	-0.7671849	9.35	-0.6078738	14.35	-0.5697472	19.35	-0.5516959
4.40	-0.7634259	9.40	-0.6072717	14.40	-0.5695042	19.40	-0.5515625
4.45	-0.7597524	9.45	-0.6066769	14.45	-0.5692628	19.45	-0.5514299
4.50	-0.7561623	9.50	-0.6060894	14.50	-0.5690232	19.50	-0.5512979
4.55	-0.7526535	9.55	-0.6055088	14.55	-0.5687852	19.55	-0.5511665
4.60	-0.7492241	9.60	-0.6049352	14.60	-0.5685489	19.60	-0.5510359
4.65	-0.7458721	9.65	-0.6043683	14.65	-0.5683142	19.65	-0.5509059
4.70	-0.7425955	9.70	-0.6038080	14.70	-0.5680812	19.70	-0.5507766
4.75	-0.7393926	9.75	-0.6032543	14.75	-0.5678497	19.75	-0.5506479
4.80	-0.7362615	9.80	-0.6027069	14.80	-0.5676198	19.80	-0.5505199
4.85	-0.7332004	9.85	-0.6021658	14.85	-0.5673914	19.85	-0.5503925
4.90	-0.7302076	9.90	-0.6016308	14.90	-0.5671646	19.90	-0.5502658
4.95	-0.7272814	9.95	-0.6011018	14.95	-0.5669394	19.95	-0.5501397
5.00	-0.7244203	10.00	-0.6005787	15.00	-0.5667156	20.00	-0.5500143

For computer users, there is a Fortran deck of the table available on loan from the Culham Laboratory