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density over the experimental range studied here and for the experimental accuracy of the data presented herein.

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Study of Some Solutions of the One-Electron-Two-Center Problem for Heteronuclear Cases*

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The Schrödinger equation for two nuclei and one electron has been solved for the first eight σ states of the system HeH^{2+} , He_2^{3+} , LiH^{3+} , and LiHe^{4+} . The resulting solutions are described and some of their properties are discussed.

I. INTRODUCTION

THE solutions of the hydrogenlike atom problem in quantum mechanics occupy a very important position in the theory of the structure of complex atoms. This is due in part to the relative simplicity of the functional forms in this case, of course. A similar situation has not developed with the theory of diatomic molecules based upon solutions of the one-electron-two-nucleus problem. Without doubt, the complexity of these functions has been a deterrent to such investigations, but the present development of computing machinery makes such difficult situations tractable, at least numerically.

The simplest two-center system, H_2^+ , has been investigated with various numerical techniques and forms of solution; some of the results are compared by De Carlo and Griffing.¹ The earlier treatments give calculations of the ground-state energy only. More recently, Bates *et al.*² obtained solutions for 10 of the lower states (eight σ and two π states) of H_2^+ ; they included tables of expansion coefficients and the energies for each of these states.

This article is a report of work done to obtain eigen-

values and eigenfunctions for some of the cases with higher and differing nuclear charges.

II. SOLUTION OF SCHRÖDINGER'S EQUATION

An excellent review of the studies made on the one-electron-two-center problem is provided by an article by Buckingham.³ We give here only a brief outline of the development of the solutions of the present problem.

Schrödinger's equation for the motion of one electron in the field to two infinitely massive nuclei is

$$-\frac{1}{2}\nabla^2\psi - \left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2} - \frac{Z_1Z_2}{\rho}\right)\psi = E\psi \quad (1)$$

in atomic units, where r_1 and r_2 refer to the distances between the electron and the nucleus of charge Z_1 and Z_2 , respectively, and ρ refers to the distance between nuclei. As is well known, the introduction of ellipsoidal coordinates allows the separation of variables in (1) and

$$\psi(\eta, \xi, \phi) = T(\eta)S(\xi)\Phi(\phi). \quad (2)$$

The separated differential equations are⁴

$$\frac{d}{d\eta} \left[(1-\eta^2) \frac{dT}{d\eta} \right] - \left(\epsilon\eta^2 + \rho\Delta\eta + \frac{m^2}{1-\eta^2} \right) T = -\lambda T, \quad (3)$$

$$\frac{d}{d\xi} \left[(\xi^2-1) \frac{dS}{d\xi} \right] + \left(\epsilon\xi^2 + \rho\Sigma\xi - \frac{m^2}{\xi^2-1} \right) S = \lambda S, \quad (4)$$

³ R. A. Buckingham, *Quantum Theory*, D. R. Bates, Ed. (Academic Press Inc., New York, 1961), Vol. 1.

⁴ W. G. Baber and H. R. Hasse, *Proc. Cambridge Phil. Soc.* **31**, 564 (1935).

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¹ V. De Carlo and V. Griffing, *J. Phys. Chem.* **66**, 845 (1962).

² D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc. (London)* **A246**, 215 (1953).

and

$$d^2\Phi/d\phi^2 = -m^2\Phi, \quad (5)$$

where

$$\epsilon = \rho^2 E_e / 2,$$

$$E_e = E - (Z_1 Z_2 / \rho),$$

$$\Delta = Z_1 - Z_2, \quad (Z_1 \geq Z_2),$$

and

$$\Sigma = Z_1 + Z_2.$$

In this study we have used

$$S(\xi) = (\xi^2 - 1)^{|m|/2} \exp(-\alpha\xi) \left(\frac{2}{\xi+1} \right)^s \sum_{k=0}^{\infty} b_k \left(\frac{\xi-1}{\xi+1} \right)^k \quad (6)$$

and

$$T(\eta) = \sum_{l=0}^{\infty} a_l \Theta_l^m(\eta), \quad (7)$$

where the $\Theta_l^m(\eta)$ are normalized associated Legendre orthogonal functions. The expression (6) is due to Jaffe.⁵ Introduction of (6) and (7) into (3) and (4) leads to two recursion relations, one for the coefficients a_l and one for the coefficients b_k . These may be treated as matrix eigenvalue problems and simultaneous solu-

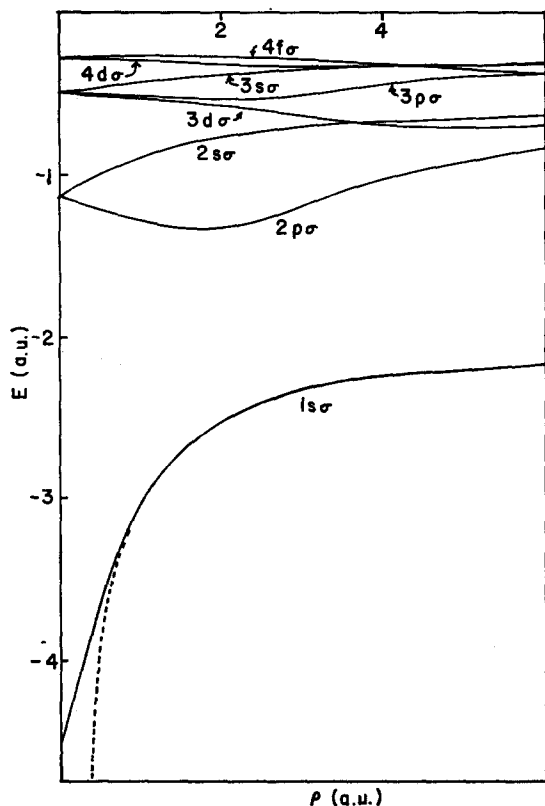


FIG. 1. First eight σ state electronic energies as functions of the internuclear distance for HeH^{2+} . The dashed line is calculated with (8).

⁵ G. Jaffe, *Fortschr. Physik* **87**, 535 (1934).

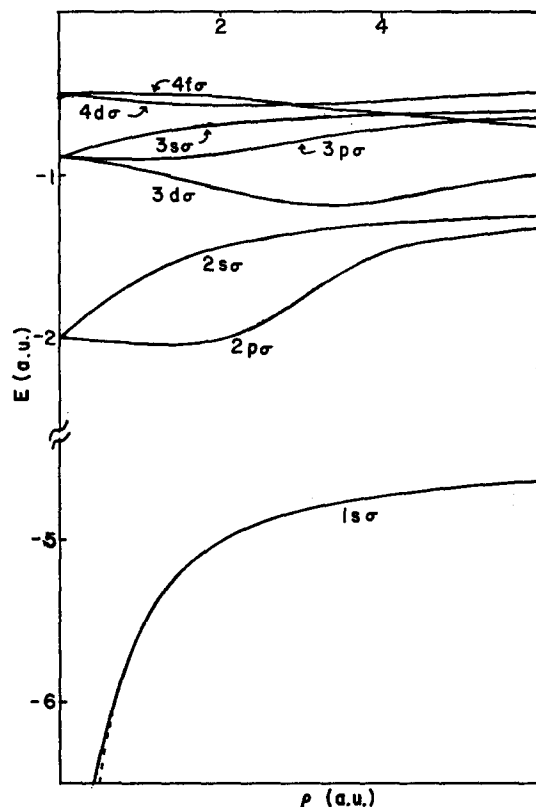


FIG. 2. First eight σ state electronic energies as functions of the internuclear distance for LiH^{2+} . The dashed line is calculated with (8).

tion for ϵ and λ leads to the eigenvalues of (1). The states of the system may be given designations which correlate with the limiting case of the united atom. The present article follows the system given originally by Bates *et al.*²

Calculations of $E_e(\rho)$ have been carried out for the systems HeH^{2+} , He_2^{3+} , and LiHe^{4+} , and the curves for the first eight σ states of each case is shown in Figs. 1 through 4. We have plotted E_e rather than the total energy, since addition of the term $Z_1 Z_2 / \rho$ obscures both the ordering and the limiting values of the levels for small ρ values.

Tables I, II, and III give our results for ϵ , λ , a_l , and b_k for HeH^+ at the respective ρ values of 2.00, 4.00, and 6.00 a.u. Numerical results for the other cases can be obtained through University Microfilm Service.⁶

Bates and Carlson⁷ suggest the inclusion of the factor $\exp[-(-\epsilon)^{1/2}]$ in the function $T(\eta)$ for the heteronuclear cases, which transforms the recursion relation for the coefficients a_l into one involving only three terms. Table IV compares our results with those of Bates and Carlson for the $1s\sigma$ state of HeH^{2+} at $\rho = 2.00$ a.u.

⁶ L. Y. Wilson, Ph.D. thesis, University of Nebraska, 1964.

⁷ D. R. Bates and T. R. Carlson, *Proc. Roy. Soc. (London)* **A234**, 207 (1956).

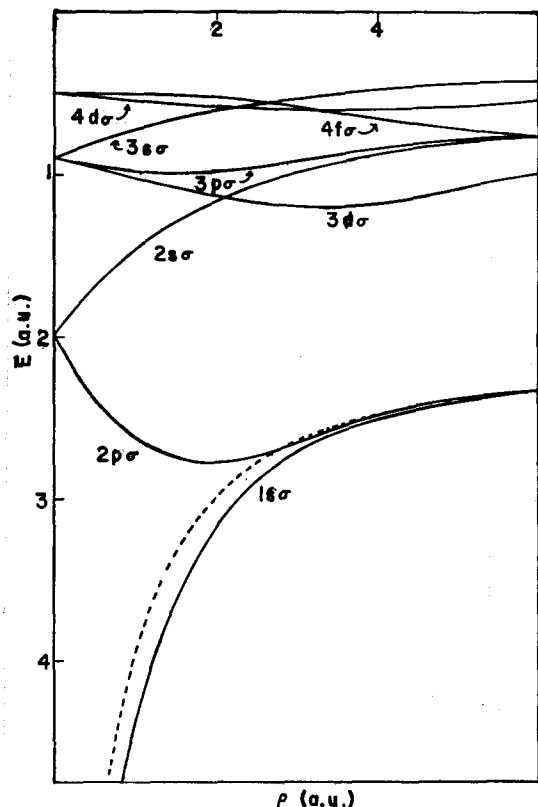


FIG. 3. First eight σ state electronic energies as functions of the internuclear distance for He_2^{3+} . The dashed line is calculated with (8).

As can be seen the rate of convergence is very close to the same in the two cases at this internuclear distance. For large ρ values the exponential factor should improve the convergence rate significantly.

III. DISCUSSION

Examination of (3) and (4) shows that ϵ and λ depend only upon $\rho\Delta$ and $\rho\Sigma$ not upon ρ , Δ , and Σ separately. Introduction of the variables $\rho' = \rho\Sigma$ and $\xi = \Delta/\Sigma$ allows one to write $\epsilon_i = \epsilon_i(\rho', \xi)$ and $\lambda_i = \lambda_i(\rho', \xi)$. Hence $E_i/\Sigma^2 = (2/\rho'^2)\epsilon_i$ and is a function of ρ' and ξ only. This fact allows one to scale the results from one set of ρ , Z_1 , and Z_2 to another. The scaling for the special case $\Delta=0$ was originally pointed out by Bates *et al.*²

Baber and Hasse⁴ derived an asymptotic expression for the total ground-state energy of a one-electron-two-nucleus system. If their formula is rewritten for the electronic energy only, one has

$$E_e = -(Z_1^2/2) - (Z_2/\rho); \quad Z_1 \geq Z_2, Z_1 \neq 1. \quad (8)$$

The physical interpretations of (8) may be clarified

by use of the virial theorem,⁸

$$2\bar{T}_e = -\bar{V}_e - \rho(dE_e/d\rho). \quad (9)$$

One easily obtains

$$\bar{T}_e = \frac{1}{2}Z_1^2,$$

and

$$\bar{V}_e = -Z_1^2 - (Z_2^2/\rho).$$

It is evident that (8) represents the energy of a normal hydrogenlike atom of nuclear charge Z_1 , plus the Coulombic energy of the electron with a nucleus of charge Z_2 at an average reciprocal distance of $1/\rho$. The original derivation indicates that (8) holds for large values of ρ . The dashed lines in Figs. 1 through 4 show (8) plotted for the respective nuclear charges. It is of interest that the deviations of (8) from the exact energy are less than 0.5% for $\rho=2$ for each of the heteronuclear cases. This indicates that the nucleus of smaller charge has very little influence on the shapes

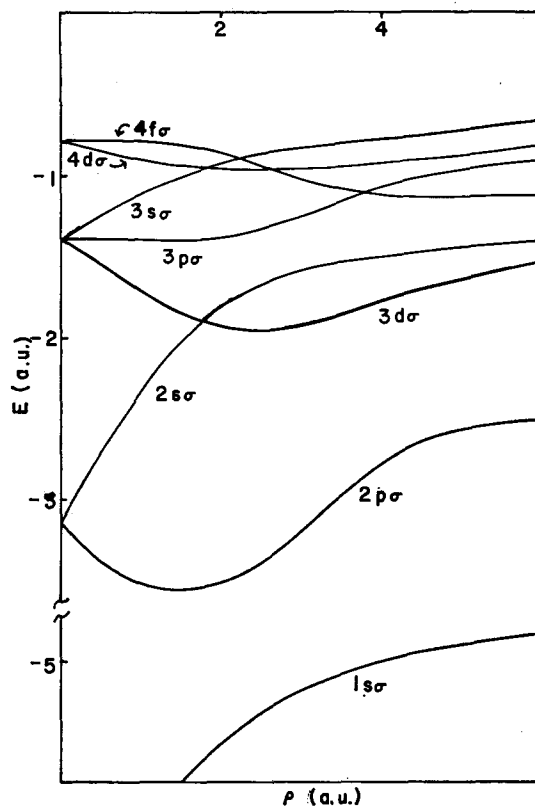


FIG. 4. First eight σ state electronic energies as functions of the internuclear distance for LiHe^{4+} . Results calculated with (8) are indistinguishable from the $1s$ values on this graph.

⁸ See, e.g., J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., Inc., New York, 1963).

TABLE I. Calculated values for HeH^{2+} at $\rho=2.00$ a.u.

	$1s\sigma$	$2p\sigma$	$2s\sigma$	$3d\sigma$	$3p\sigma$	$3s\sigma$	$4d\sigma$	$4f\sigma$
ϵ	-5.02435	-2.69037	-1.57419	-1.14252	-1.07325	-0.077761	-0.62083	-0.57805
λ	-3.15781	0.95642	-1.27218	5.49329	1.75924	-0.89809	5.76684	11.7491
a_l $l=0$	-0.7482	0.5626	0.8562	-0.00729	0.4919	0.8788	0.0187	-0.0022
1	0.5930	0.8131	-0.4945	0.2456	0.8442	-0.4645	0.2497	0.0022
2	-0.2835	-0.1293	0.1463	0.9561	-0.2076	0.1079	0.9544	0.1673
3	0.0870	0.0734	-0.0286	-0.1569	0.0468	-0.0165	-0.1607	0.9781
4	-0.0222	-0.0094	0.0043	0.0316	-0.0059	0.0019	0.0227	-0.1227
5	0.0048	0.0022	-0.0005	-0.0032	0.0007	-0.0002	-0.0020	0.0149
6	-0.0008	-0.0002	...	0.0003	0.9002	-0.0011
7	0.0001	0.0001
b_k $k=0$	0.9999	0.9952	-0.2133	0.7182	-0.3143	0.0900	-0.4664	0.1744
1	0.0112	0.0978	0.9768	0.6944	0.9401	-0.6085	0.3936	0.8550
2	0.0002	0.0002	0.0194	0.0440	2.1323	0.7884	0.7964	0.4875
3	0.0004	0.0001	0.0001	0.1794	0.0529	0.0304
4	0.0004	0.0001	0.0001

TABLE II. Calculated values for HeH^{2+} at $\rho=4.00$ a.u.

	$1s\sigma$	$2p\sigma$	$2s\sigma$	$3d\sigma$	$3p\sigma$	$3s\sigma$	$4d\sigma$	$4f\sigma$
ϵ	-18.0048	-8.24865	-5.44790	-5.65492	-3.59456	-2.74822	-2.73541	-2.58465
λ	-14.0677	-0.79971	-4.92582	3.37958	1.27548	-3.23590	4.89961	10.8624
a_l $l=0$	-0.5078	0.7354	0.6635	-0.0989	0.7095	0.7236	0.0641	-0.0213
1	0.6500	0.6560	-0.6562	0.4043	0.6220	-0.6330	0.4575	0.0003
2	-0.4834	0.0329	0.3372	0.8624	-0.2971	0.2644	0.8393	0.3255
3	0.2653	0.1650	-0.1199	-0.2542	0.1423	-0.0741	-0.2731	0.9162
3	0.2653	0.1650	-0.1199	-0.2542	0.1423	-0.0741	-0.2731	0.9162
4	-0.1164	-0.0178	0.0328	0.1325	-0.0341	0.0156	0.0853	-0.2245
5	0.0425	0.0145	-0.0073	-0.0272	0.0075	-0.0026	-0.0154	0.0600
6	-0.0133	-0.0018	-0.0014	0.0069	-0.0012	0.0004	0.0025	-0.0090
7	0.0036	0.0006	0.0002	-0.0011	0.0002	...	-0.0003	0.0013
8	-0.0009	-0.0001	...	0.0002	-0.0001
9	0.0002
b_k $k=0$	0.9999	0.9946	-0.1184	0.9661	-0.1769	0.0386	-0.2453	0.4485
1	0.0112	0.1034	0.9926	0.2582	0.9732	-0.4549	0.9040	0.8656
2	0.0002	0.0000	0.0271	0.0033	0.1368	0.8891	0.3501	0.2229
3	0.0002	...	0.0002	0.0331	0.0075	0.0052
4	0.0002

TABLE III. Calculated values for HeH^{2+} at $\rho=6.00$ a.u.

	$1s\sigma$	$2p\sigma$	$2s\sigma$	$3d\sigma$	$3p\sigma$	$3s\sigma$	$4d\sigma$	$4f\sigma$
ϵ	-39.0030	-15.2252	-11.3887	-12.5672	-6.5672	-6.92790	-5.73817	-6.9337
λ	-33.0438	-3.60955	-10.7514	0.06034	0.47842	-6.70301	3.57054	8.94625
a_l $l=0$	-0.4105	0.6778	0.5499	-0.2934	0.7820	0.6199	0.1705	-0.0963
1	0.5908	0.6419	-0.6654	0.4249	0.4145	-0.6715	0.6208	-0.0331
2	-0.5316	0.2710	0.4476	0.7256	-0.3604	0.3762	0.6830	0.4691
3	0.3729	0.2319	-0.2167	-0.3488	0.2757	-0.1458	-0.3051	0.8195
4	-0.2164	0.0156	0.0823	0.2765	-0.0985	0.0431	0.1559	-0.2800
5	0.1072	0.0332	-0.0257	-0.0876	0.0309	-0.0103	-0.0410	0.1362
6	-0.0462	-0.0013	0.0068	0.0328	-0.0071	0.0021	0.0102	-0.0313
7	0.0177	0.0025	-0.0016	-0.0077	0.0015	-0.0004	-0.0019	0.0077
8	-0.0061	-0.0002	0.0003	0.0020	-0.0003	0.0001	0.0003	-0.0013
9	0.0019	0.0001	-0.0001	-0.0004	0.0002
10	-0.0005
11	0.0001
b_k $k=0$	0.9999	0.9937	-0.0811	0.9844	-0.1261	0.0212	-0.1499	0.8069
1	0.0075	0.1124	0.9963	0.1760	0.9773	-0.3582	0.9509	0.5878
2	...	0.0003	0.0277	0.0017	0.1701	0.9325	0.2706	0.0589
3	0.0001	...	0.0011	0.0404	0.0053	0.0003
4	0.0001

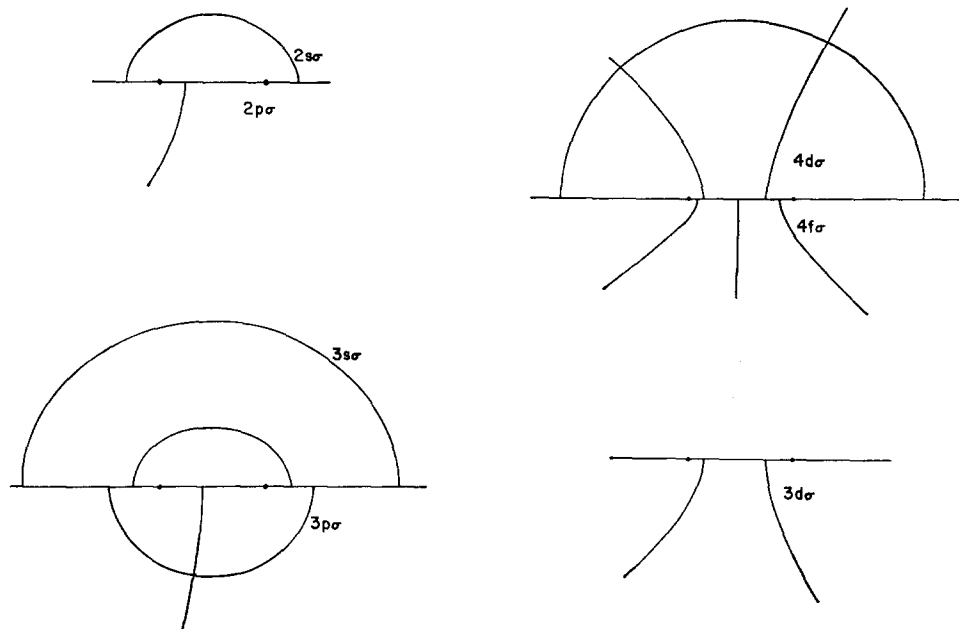


FIG. 5. The nodal surfaces for the first eight σ states of HeH^{2+} at $\rho=2.00$ a.u.

of the wavefunction even at fairly small internuclear distances in these cases. The situation for He_2^{3+} is different. With this homonuclear case a resonance effect is possible, and there is the larger deviation of 6% at $\rho=2$ between (8) and the exact energy.

TABLE IV. Comparison of expansion coefficients for the present form and the exponentially modified form of the η solution for an internuclear distance of two atomic units.

l	a_l^a	a_l^b
0	1.0000	1.0000
1	-1.37280	0.86374
2	0.84721	0.53979
3	-0.30744	0.26884
4	0.08889	0.11105
5	-0.01937	0.03909
6	0.00367	0.01197
7	-0.00057	0.00324
8	0.00008	0.00008
9	-0.00001	0.00002

^a From solution of (7). These have been modified to the coefficients for unnormalized associated Legendre functions for direct comparison.

^b From Bates and Carson.⁷

In spite of the small effect on the average kinetic energy of the electron the presence of the second nucleus has a profound effect on the shapes of the nodal surfaces of ψ . This follows immediately from the form of ψ . Restricting the discussion to σ states, it is seen that the nodal surfaces are coordinate surfaces of the ellipsoidal system determined by $S(\xi)=0$ and $T(\eta)=0$. Hence the nodal surfaces are ellipsoids of revolution and one sheet of hyperboloids of revolution of two sheets. Figure 5 shows the intersections of the nodal surfaces with the $x-z$ plane for the $2s\sigma$, $2p\sigma$, $3s\sigma$, $3p\sigma$, $3d\sigma$, $4d\sigma$, and $4f\sigma$ states of HeH^{2+} at $\rho=2.00$ a.u. It is interesting that, in spite of what might be expected, the ellipsoidal nodes are symmetric with respect to reflections $z \rightarrow -z$ (z axis along the internuclear line) even for the heteronuclear cases and regardless of the value of ρ . The positions of the hyperboloidal nodes depend strongly on Δ , of course.

Examination of Table I shows that λ approaches the eigenvalues of the total angular momentum operator as the electronic energy increases. Similar behavior is exhibited by the other systems as may be seen from Ref. 6.