APPENDIX II

Wave Functions

$$\mathbf{P}=\tfrac{1}{2}(I-i),^{13}$$

$$(ab:c)\equiv\det[a(1)\alpha(1)b(2)\alpha(2)c(3)\beta(3)],$$

$$[(ac)b]\equiv(ab:c)+(cb:a),$$

$$\Phi_1=\mathbf{P}[(1s_a1s_a)1s_b'],$$

$$\Phi_2=\mathbf{P}[(2s_a2s_a)1s_b'],$$

$$\Phi_3=\mathbf{P}[(3s_a3s_a)1s_b'],$$

$$\Phi_4=2\mathbf{P}[(1s_a2s_a)1s_b'],$$

$$\Phi_5=2\mathbf{P}[(1s_a3s_a)1s_b'],$$

$$\Phi_6=2\mathbf{P}[(2s_a3s_a)1s_b'],$$

$$\Phi_7=2\mathbf{P}[(2s_a1s_b')1s_a],$$

$$\Phi_8=\mathbf{P}[(1s_a1s_a)2s_a],$$

$$\Phi_9=\mathbf{P}[(1s_a1s_a)3s_a],$$

$$\Phi_{10}=\mathbf{P}[(2p_{0a}2p_{0a})1s_b'],$$

$$\Phi_{11}=2\mathbf{P}[(2p_{+1a}2p_{-1a})1s_b'],$$

$$\Phi_{12}=\mathbf{P}[(1s_a1s_a)2p_{0a}],$$

$$\Phi_{13}=2\mathbf{P}[(1s_a2p_{0a})1s_b'],$$

$$\Phi_{14}=2\mathbf{P}[(2s_a2p_{0a})1s_b'],$$

$$\Phi_{15}=\mathbf{P}[(1s_a1s_a)2s_b],$$

$$\Phi_{16}=\mathbf{P}[(1s_a1s_a)3s_b],$$

$$\Phi_{17}=\mathbf{P}[(3p_{0a}3p_{0a})1s_b'],$$

$$\Phi_{18}=2\mathbf{P}[(3p_{+1a}3p_{-1a})1s_b'],$$

$$\Phi_{19}=2\mathbf{P}[(2p_{0a}3p_{0a})1s_b'],$$

$$\Phi_{20}=2\mathbf{P}\{[(2p_{-1a}3p_{+1a})1s_b']+[(2p_{+1a}3p_{-1a})1s_b']\},$$

$$\Phi_{21}=\mathbf{P}[(3d_{0a}3d_{0a})1s_b'],$$

$$\Phi_{22}=2\mathbf{P}[(3d_{+1a}3d_{-1a})1s_b'],$$

$$\Phi_{23}=2\mathbf{P}[(3d_{+2a}3d_{-2a})1s_b'],$$

$$\Phi_{24}=2\mathbf{P}[(1s_a3p_{0a})1s_b'],$$

$$\Phi_{25}=2\mathbf{P}[(1s_a3d_{0a})1s_b'],$$

$$\Phi_{26}=2\mathbf{P}[(2s_a3p_{0a})1s_b'].$$

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[13] The operator **P** produces the ungerade symmetry. I is the identity transformation and i is the inversion through the center of the molecule.

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Potential Curve of the Metastable Helium Molecule*

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The potential curve of the $He_2(^3\Sigma_u^+)$ molecule was computed using a twelve-term function containing orbitals through $3d$. The curve shows a potential maximum near 4.5 a_0 which lies 0.081 eV above the calculated energy of the separated atoms. A similar maximum was obtained in two previous calculations which used a more restricted basis set. The maximum appears to be supported by experiment. In this calculation, $E_{\mathrm{exp}}(\mathrm{atoms})-E_{\mathrm{calc}}(r_e)=0.94$ eV and $E_{\mathrm{calc}}(\mathrm{atoms})-E_{\mathrm{calc}}(r_e)=1.24$ eV.

INTRODUCTION

The potential curve of $^3\Sigma_u^+$ He_2 (He_2^*) using simple one-configuration wave functions has been computed by Buckingham and Dalgarno[1] and Brigman, Brient, and Matsen.[2] Both calculations show a potential maximum near $4a_0$ (a_0= first Bohr radius) which is a feature of considerable experimental interest. The present calculations extend the work of Brigman, Brient, and Matsen by adding polarization to the wave function. The calculations were performed using the CDC 1604 computer at the Computation Center at The University of Texas, and programs[3] written by members of the Molecular Physics Group at The University of Texas.

WAVE FUNCTIONS

The wave functions used in these calculations are constructed from Slater atomic orbitals. The $^3\Sigma_u^+$ symmetry is achieved by forming bond functions[4] from Slater determinants, and projecting the result with

$$\mathbf{P}=\tfrac{1}{4}(\mathbf{E}+\boldsymbol{\sigma}_v)(\mathbf{E}-\mathbf{i}). \tag{1a}$$

Here **E** is the identity transformation, $\boldsymbol{\sigma}_v$ is a reflection in a plane containing the molecular axis, and **i** is an inversion through the center of the molecule.

The bond functions have the form

$$[(ab)cd]\equiv(ac:bd)+(bc:ad)+(ad:cb)+(bd:ca), \tag{1b}$$

where

$$(ab:cd)\equiv\det[a(1)\alpha(1)b(2)\alpha(2)c(3)\beta(3)d(4)\beta(4)]. \tag{1c}$$

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TABLE I. The configurations of the closed-shell wave function.

$$\psi_1=\mathbf{P}[(1s_a1s_a)2s_b'1s_b']$$
$$\psi_2=2\mathbf{P}[(1s_a2s_a)2s_b'1s_b']$$
$$\psi_3=\mathbf{P}[(2s_a2s_a)2s_b'1s_b']$$
$$\psi_4=\mathbf{P}[(2p_{0a}2p_{0a})2s_b'1s_b']$$
$$\psi_5=2\mathbf{P}[(2p_{+1a}2p_{-1a})1s_b'2s_b']$$
$$\psi_6=\mathbf{P}[(1s_a1s_a)3s_b'2s_b']$$
$$\psi_7=\mathbf{P}[(1s_a1s_a)2p_{0b}'1s_b']$$
$$\psi_8=\mathbf{P}[(3d_{0a}3d_{0a})1s_b'2s_b']$$
$$\psi_9=2\mathbf{P}\{-[(3d_{-1a}3d_{+1a})1s_b'2s_b']+[(3d_{-2a}3d_{+2a})1s_b'2s_b']\}$$
$$\psi_{10}=2\mathbf{P}[(1s_a2p_{0a})1s_b'2s_b']$$
$$\psi_{11}=\mathbf{P}[(1s_a1s_a)2s_a1s_b']$$
$$\psi_{12}=\mathbf{P}[(1s_a1s_a)2p_{0a}1s_b']$$

TABLE II. Closed-shell orbital exponents.

Orbital	$R<4.0$	$R\geqq 4.0$
$\delta(1s)$	1.420 0	1.420 0
$\delta(1s')$	1.997 9	1.994 8
$\delta(2s)$	1.848 8	1.843 5
$\delta(2s')$	0.563 7	0.563 7
$\delta(2p_{+1})=\delta(2p_{-1})$	2.522 0	2.482 0
$\delta(2p_0)$	2.462 0	2.462 0
$\delta(2p_0')$	0.564 6	0.564 6
$\delta(3s)$	1.227 0	1.227 0
$\delta(3d_{+2})=\delta(3d_{-2})$	3.629 0	3.629 0
$\delta(3d_0)$	3.609 0	3.609 0
$\delta(3d_{-1})=\delta(3d_{+1})$	3.629 0	3.629 0

Calculations were performed using two types of wave function; an open-shell wave function with nine configurations, and a closed-shell wave function with twelve configurations,

$$\psi=\sum_{i=1}^{12} c_i\psi_i. \tag{2}$$

The configurations of the closed-shell wave function are listed in Table I using the notation of Eqs. (1) and (2), and the conventional notation for the Slater atomic orbitals.

RESULTS

Partial optimization of nonlinear parameters was carried out on (2) and on the open-shell wave function at several internuclear separations. The resulting orbital exponents for the closed-shell wave function are given in Table II. The eigenvector of linear coefficients and the corresponding eigenvalue of the secular equation are shown in Table III. When the internuclear separation is increased without limit, the wave functions approach a triplet helium atom wave function and a singlet helium atom wave function. The resulting total separated atom energies for the closed-shell and open-shell wave functions are -5.06960 and -5.07071 a.u., respectively (1 a.u.$=27.21$ eV). These results are depicted in Fig. 1 where the potential energy is drawn as a smooth curve through the points calculated with the closed-shell wave function. As may be seen from Fig. 1 the energy computed from the open-shell wave function is higher than that with the closed-shell wave function at internuclear separations less than 5 a_0. For this reason and because the closed-shell function re-

TABLE III. Eigenvalues and eigenvectors for closed-shell wave functions.

R	1.500	1.800	1.900	2.015	2.130	2.245	2.360	2.500
E	−5.009 80	−5.093 92	−5.104 92	−5.111 47	−5.113 46	−5.112 40	−5.109 46	−5.104 43
c_1	+0.958 861	+0.848 926	+0.824 883	+0.802 768	+0.785 154	+0.771 204	+0.760 227	+0.749 872
c_2	−0.223 369	−0.136 878	−0.116 702	−0.097 330	−0.081 123	−0.067 554	−0.056 285	−0.045 004
c_3	−0.065 370	−0.122 610	−0.136 113	−0.149 304	−0.160 593	−0.170 370	−0.178 757	−0.187 502
c_4	−0.023 205	−0.019 302	−0.018 731	−0.018 307	−0.018 050	−0.017 895	−0.017 824	−0.017 784
c_5	−0.018 143	−0.017 572	−0.017 457	−0.017 361	−0.017 292	−0.017 248	−0.017 216	−0.017 198
c_6	+0.020 113	+0.012 590	+0.010 795	+0.009 020	+0.007 518	+0.006 276	+0.005 163	+0.004 099
c_7	−0.013 410	−0.018 983	−0.018 772	−0.017 393	−0.014 913	−0.011 460	−0.007 149	−0.001 108
c_8	+0.003 144	+0.003 129	+0.003 094	+0.003 050	+0.003 008	+0.002 969	+0.002 935	+0.002 900
c_9	+0.003 017	+0.002 929	+0.002 903	+0.002 875	+0.002 852	+0.002 831	+0.002 814	+0.002 797
c_{10}	−0.018 006	−0.018 720	−0.018 335	−0.017 702	−0.016 923	−0.016 046	−0.015 103	−0.013 916
c_{11}	−0.089 083	−0.098 758	−0.100 486	−0.101 493	−0.101 508	−0.100 638	−0.098 936	−0.096 045
c_{12}	−0.005 559	−0.005 510	−0.005 311	−0.004 952	−0.004 465	−0.003 877	−0.003 218	−0.002 371

R	3.000	3.500	4.000	4.500	5.000	5.500	6.000	15.000
E	−5.085 03	−5.072 35	−5.066 42	−5.064 50	−5.064 55	−5.065 28	−5.066 38	−5.069 72
c_1	+0.729 881	+0.723 627	+0.722 800	+0.722 749	+0.722 462	+0.721 617	+0.720 510	+0.715 809
c_2	−0.020 746	−0.011 664	−0.009 919	−0.009 354	−0.009 326	−0.009 319	−0.009 311	−0.009 169
c_3	−0.207 838	−0.216 212	−0.217 235	−0.217 429	−0.216 992	−0.216 489	−0.216 018	−0.214 684
c_4	−0.017 807	−0.017 828	−0.017 875	−0.017 927	−0.017 972	−0.018 004	−0.018 027	−0.018 056
c_5	−0.017 224	−0.017 305	−0.017 637	−0.017 731	−0.017 808	−0.017 864	−0.017 898	−0.017 938
c_6	+0.002 069	+0.001 664	+0.002 412	+0.002 475	+0.002 495	+0.002 431	+0.002 282	+0.001 746
c_7	+0.021 966	+0.037 001	+0.040 573	+0.036 602	+0.029 570	+0.022 335	+0.016 143	−0.000 000
c_8	+0.002 825	+0.002 798	+0.002 794	+0.002 799	+0.002 807	+0.002 814	+0.002 819	+0.002 825
c_9	+0.002 765	+0.002 760	+0.002 768	+0.002 780	+0.002 791	+0.002 799	+0.002 805	+0.002 811
c_{10}	−0.009 767	−0.006 511	−0.004 217	−0.002 741	−0.001 791	−0.001 154	−0.000 751	−0.000 000
c_{11}	−0.082 191	−0.069 031	−0.058 767	−0.050 237	−0.042 832	−0.036 169	−0.030 217	−0.000 489
c_{12}	+0.000 296	+0.001 760	+0.002 233	+0.002 230	+0.002 023	+0.001 753	+0.001 489	+0.000 031

TABLE IV. Properties of $^3\Sigma_u^+$ He_2

Property	Calculated	Experimental
Potential energy	-14.7417 a.u.	$\cdots$
Kinetic energy	$+5.1336$ a.u.	$\cdots$
Value of the wave function at the atomic nuclei	$3.1426\ (a_0)^{-3}$	$\cdots$
$\langle Z^2\rangle$	$13.7540\ (a_0)^2$	$\cdots$
Quadrupole moment	$7.6248\ (a_0)^2$	$\cdots$
r_e	$2.139(a_0)$	$1.981a_0$
D_e	See text	(2.6) eV
ω_e	1743.4 cm^{-1}	1811.2 cm^{-1}
$\omega_e x_e$	91.7 cm^{-1}	39.2 cm^{-1}
B_e	6.6 cm^{-1}	7.66 cm^{-1}
α_e	0.26 cm^{-1}	0.131 cm^{-1}

quires less computing time, we do not present the results from the open-shell function in detail.

In the course of these calculations, the work of Brigman, Brient, and Matsen[2] was repeated. Large discrepancies were found at small internuclear separations, but in the neighborhood of the hump the discrepancies are negligible. Figure 1 shows these corrected results, labeled BB&M. The highest curve in Fig. 1 is that computed by Buckingham and Dalgarno and is labeled B&D.

Table IV contains several molecular properties as computed from the present closed-shell wave function and, where available, the experimental results[5] for these same properties. A third-order polynomial was fitted to the potential energy curve in the neighborhood of the minimum to find the values of spectroscopic constants reported in Table IV.

DISCUSSION

According to the variation theorem, the quantity $E_{\mathrm{exp}}(\mathrm{atoms})-E_{\mathrm{calc}}(r_e)$ ($=0.939$ eV from our calculation) is a rigorous lower bound for the dissociation energy of He_2^*. The calculations produced a rationalized binding energy, $E_{\mathrm{calc}}(\mathrm{atoms})-E_{\mathrm{calc}}(r_e)$ of 1.24 eV for the closed-shell wave function and 1.08 eV for the open-shell wave function.

Meyerott[6] has estimated the binding energy to be 1.70 eV by the relation $D_e(He_2^*)=D_e(He_2^+)+I(He_2^*)-I(He^*)$. The last two quantities are determined experimentally to be 4.25 and 4.77 eV, respectively. For $D_e(He_2^+)$ Meyerott[6] used the rationalized binding energy of 2.20 eV calculated by Weinbaum to obtain $D_e(He_2^*)=1.70$ eV. Recently, Reagan, Browne, and Matsen[7] established a rigorous lower limit of 2.24 eV for the former quantity. This permits the establishment of a lower limit of 1.76 eV for the dissociation energy of the metastable helium molecule. We see that, although our calculation is a considerable improvement over the two previous calculations which employed more restricted basis sets, it is still far short of being an acceptable energy calculation. The agreement with experimental spectroscopic constants is fair.

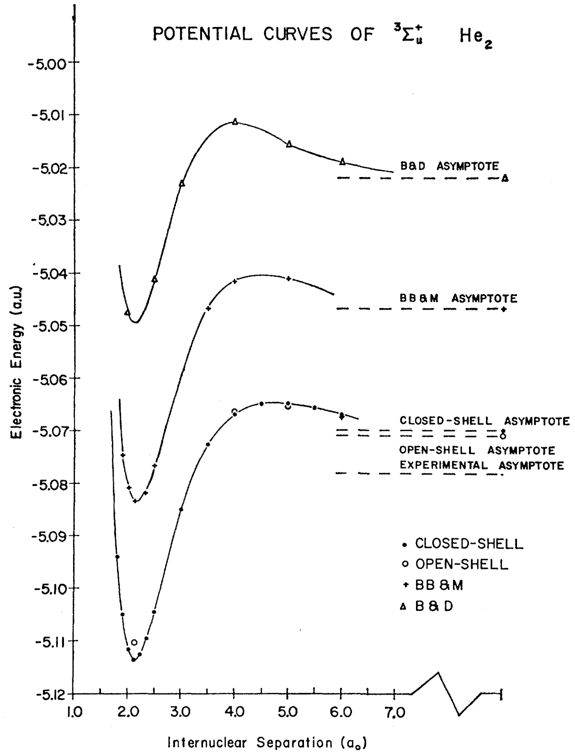

FIG. 1. Potential curves of $^3\Sigma_u^+$ He_2.

The calculation yields a maximum at 4.5 a_0 in the potential curve which lies 0.081 eV above the calculated energy of the separated atoms. A maximum similar to this has been obtained in the two previous calculations. The experimental arguments for its existence are based on the temperature coefficients of the diffusion of triplet helium atom through helium atoms and the rate constant for the process $He(^3S)+2He\rightarrow He_2^*+He$. Recently,[8] it has been shown that the rate constant for the process $^4He(^3S)+{}^3He\rightarrow {}^4He+{}^3He(^3S)$ goes to zero at liquid-helium temperatures, which fact provides additional experimental support for the existence of the hump.

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