

support of ideas such as those of Zener,<sup>9</sup> expressed more recently in a somewhat different form by Goodenough,<sup>10</sup> that ferromagnetic interactions in the transition metals cannot be attributed to direct coupling of localized orbitals. The fact that some of the Co orbitals ( $\sigma$  and  $\pi$ ), for  $Z=1$ , are indicated to be covalently coupled is consistent with the suggestion by Goodenough that

the ferromagnetic interaction might arise from indirect coupling of localized orbitals through quasi-degenerate orbitals of a metallic or antibonding  $d$  band, since any occupied  $d$  orbital beyond five per atom would have to be either an antibonding covalently coupled orbital or else an energetically unfavorable localized  $dd$  orbital with spin antiparallel to the net spin on its atom. A partially filled antibonding band is required for the ferromagnetic coupling mechanism discussed by Goodenough.

<sup>9</sup> C. Zener, Phys. Rev. **81**, 440 (1951); **83**, 299 (1951).

<sup>10</sup> J. B. Goodenough, Phys. Rev. **120**, 67 (1960).

## Repulsive Interaction between Two Ground-State Helium Atoms\*†

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(Received October 12, 1961)

The repulsion energy between two ground-state helium atoms ( $^1\Sigma_g^+$  state of  $\text{He}_2$ ) has been investigated in the single-configuration MO (molecular orbital) approximation and then further refined to include the effects of electron correlation by the inclusion of superposition of configurations. In the former case, the wave function is expressed as a single antisymmetrized spin-orbital product (ASOP) of the form  $|\sigma_g 1s(1)\alpha(1)\sigma_g 1s(2)\beta(2)\sigma_u 1s'(3)\alpha(3)\sigma_u 1s'(4)\beta(4)|$ , where the MO's  $\sigma_g 1s$  and  $\sigma_u 1s'$  are approximated as the sum and difference of Slater-type orbitals (STO's)  $1s$  and  $1s'$ , respectively, and the energy minimized with respect to the orbital exponents. In addition to the repulsion energy at small internuclear distances the slight polarization of the  $\sigma_u 1s'$  MO effected by the  $\zeta$  variation, permitted the single ASOP wave function to give indications of the van der Waals energy minimum at large distances. The superposition of configurations treatment employed a linear combina-

tion of configurations constructed out of a  $1s, 1s', 2p\sigma, 2p\pi$  STO basis set, and at five internuclear distances  $R$  between 0.5 and 2.0 Å, the STO orbital exponents were varied to minimize the energy. Various wave functions including from 10 to 64 electron configurations were tried, which were so chosen that the wave functions would go properly as  $R \rightarrow 0$  into the  $^1S$  ground-state function of beryllium and as  $R \rightarrow \infty$  go into a product of two  $^1S$  helium atom functions. The computed repulsion energies in the region  $0.5 \text{ Å} \leq R \leq 1.0 \text{ Å}$  are 2.8 to 1.2 times higher than values deduced from experimental scattering data obtained several years ago, and since the difference between the lowest computed (64-configuration) energy and the estimated exact energy is much smaller than this, a reinvestigation of the scattering analysis is emphasized.

### I. INTRODUCTION

THE exchange or repulsive interaction potential between two  $^1S$  ground-state helium atoms has been investigated by several people over the past ten years using approximate electronic wave functions of varying degrees of accuracy. The earlier calculations by Slater<sup>1</sup> and Rosen<sup>2</sup> were of the valence-bond type in which the interaction between the two atoms was treated as a perturbation, so that the molecular wave function was constructed from approximate wave functions of the individual helium atoms.

In subsequent investigations<sup>3-8</sup> the molecular orbital

approach was followed, in which the two helium atoms are regarded as a  $\text{He}_2$  molecule in which each of the four electrons is assigned to a one-electron orbital wave function, or molecular orbital (MO), which extends over the whole molecule. The MO calculations assumed that two electrons are assigned to a bonding  $1\sigma_g$  MO with opposite spins  $\alpha$  and  $\beta$  and two electrons are assigned to an antibonding MO  $1\sigma_u$ , likewise with opposed spins. The molecular wave function is then expressed as a single antisymmetrized spin-orbital product (ASOP) or Slater determinant:

$$\Psi_{\text{MO}} = (4!)^{-\frac{1}{2}} |1\sigma_g(1)\alpha(1)1\sigma_g(2)\beta(2)1\sigma_u(3) \times \alpha(3)1\sigma_u(4)\beta(4)|. \quad (1)$$

The several reported MO calculations differ formally first in the specified form of the MO's, and secondly in the treatment of the variational parameters. A sum-

\* This work was assisted by the Office of Naval Research and by a grant from the National Science Foundation.

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<sup>1</sup> J. C. Slater, Phys. Rev. **32**, 349 (1928).

<sup>2</sup> P. Rosen, J. Chem. Phys. **18**, 1182 (1950).

<sup>3</sup> V. Griffing and J. F. Wehner, J. Chem. Phys. **23**, 1024 (1955); referred to hereafter as G-W.

<sup>4</sup> M. Sakamoto and E. Ishiguro, Progr. Theoret. Phys. (Kyoto) **15**, 37 (1956).

<sup>5</sup> S. Huzinaga, (a) Progr. Theoret. Phys. (Kyoto) **18**, 140 (1957); (b) *ibid.* **20**, 15 (1958).

<sup>6</sup> T. Hasino and S. Huzinaga, Progr. Theoret. Phys. (Kyoto) **20**, 631 (1958).

<sup>7</sup> N. Moore, J. Chem. Phys. **33**, 471 (1960).

<sup>8</sup> B. J. Ransil, J. Chem. Phys. **34**, 2109 (1961).

TABLE I. Summary of calculations of He<sub>2</sub> repulsive potential. All calculations except the first two and the last are of the single ASOP type. In the former cases, the He<sub>2</sub> molecular wave function is in general expressed as a single ASOP.  $\Psi = (4!)^{-1/2} |\phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)|$ . The MO's  $\sigma_g 1s(\zeta)$ ,  $\sigma_u 1s(\zeta')$ , etc., are defined in Eqs. (2), (15), and (17) of this paper.

Author	Wave function	$R(A)$		$V(R) = ae^{-bR}$ (in ev)			
		$a$	$b$	0.5	0.625	0.75	1.0
Slater <sup>a</sup>	Valence-bond, see discussion in Sec. III	481	4.60	48.23	27.14	15.27	4.835
Rosen <sup>b</sup>	Valence-bond, see discussion in Sec. III	577	4.40	63.93	36.89	21.28	7.084
Griffing and Wehner <sup>c</sup>	$\phi_1 = \sigma_g 1s(\zeta)$ , $\phi_2 = \sigma_u 1s(\zeta')$ ; $\zeta = 1.6875$ for all $R$	Not given		44.90	25.08	14.32	4.790
Sakamoto and Ishiguro <sup>d</sup>	$\phi_1 \sim e^{-\alpha\zeta - \beta\eta}$ , $\phi_2 \sim e^{-\alpha\zeta + \beta\eta}$ , $\xi = (r_a + r_b)/R$ , $\eta = (r_a - r_b)/R$ ; $\alpha$ and $\beta$ variable parameters	409	4.47	43.76	25.03	14.31	4.682
Huzinaga <sup>e</sup>	$\phi_1 = \sigma_g 1s(\zeta)$ , $\phi_2 = \sigma_u 1s(\zeta')$ ; $\zeta$ and $\zeta'$ independently chosen	234	4.09	30.27	18.16	10.89	3.917
Hasino and Huzinaga <sup>f</sup>	$\phi_1 = 1\sigma_g = \sigma_g 1s(\zeta) + \lambda_g \sigma_g 2p(\zeta)$ , $\phi_2 = 1\sigma_u = \sigma_u 1s(\zeta) + \lambda_u \sigma_u 2p(\zeta)$ ; $\lambda_g$ and $\lambda_u$ varied to minimize energy; $\zeta = 1.6875$	Not given			21.65		
Moore <sup>g</sup>	Diagonal of ASOP given by $1s_a\alpha(1)1s_a\beta(2)1s_b\alpha(3)1s_b\beta(4)$ $\times [1 + \gamma\zeta^2(x_{a1}x_{b3} + x_{a1}x_{b4} + x_{a2}x_{b3} + x_{a2}x_{b4})$ $+ \gamma\zeta^2(y_{a1}y_{b3} + \dots) + \delta\zeta^2(z_{a1}z_{b3} + \dots)]$ ; other terms modified to maintain antisymmetrization; $\zeta = 1.6875$ ; $\gamma$ and $\delta$ varied to minimize energy	Not given			24.77		
Ransil <sup>h</sup>	$\phi_1 = 1\sigma_g = a_{1g}\sigma_g 1s(\zeta) + a_{2g}\sigma_g 2s(\zeta) + a_{2p}\sigma_g 2p(\zeta)$ , $\phi_2 = 1\sigma_u = b_{1g}\sigma_u 1s(\zeta) + b_{2g}\sigma_u 2s(\zeta) + b_{2p}\sigma_u 2p(\zeta)$ ; energy minimized with respect to $\zeta$ and coefficients at each $R$	Not given		30.84		11.34	4.104
This paper <sup>i</sup>	$\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$	191.47	3.8486	27.95 (27.76)	17.28 (17.33)	10.68 (10.78)	4.080 (4.059)

<sup>a</sup> See reference 1.

<sup>b</sup> See reference 2. The values of  $a$  and  $b$  are taken from J. Hirschfelder, C. Curtiss, and R. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1065.

<sup>c</sup> See reference 3.

<sup>d</sup> See reference 4.

<sup>e</sup> See reference 5.

<sup>f</sup> See reference 6. Interested primarily in polarization effects at large distances in the Van der Waals region. Energy value quoted computed at 0.627 Å.

<sup>g</sup> See reference 7. Remarks in footnote f also apply here.

<sup>h</sup> See reference 8.

<sup>i</sup> The energy values given in the first row were computed from  $a$  and  $b$ ; the bracketed energies of the second row are the  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  values on the basis of which  $a$  and  $b$  were obtained.

mary of previous MO calculations is presented in Table I, which includes numerical values of the repulsion energy at 0.5, 0.625, 0.75, and 1.0 Å.

A comparison of these results indicates that the lowest energies are those of Huzinaga<sup>5a</sup> and Ransil.<sup>8</sup> The former approximated the  $1\sigma_g$  and  $1\sigma_u$  MO's as the sum and difference of  $1s$  Slater-type orbitals (STO's) around nuclear centers  $a$  and  $b$ :

$$\begin{aligned} 1\sigma_g &= \sigma_g 1s = N_g [1s_a + 1s_b], \\ 1\sigma_u &= \sigma_u 1s' = N_u' [1s_a' - 1s_b'], \end{aligned} \quad (2)$$

where  $N_g$ ,  $N_u'$  are the appropriate normalization factors, and  $1s = (\zeta^3/\pi)^{1/2} \exp(-\zeta r)$ . In this approximation, then, the wave function is represented by the electron configuration  $(\sigma_g 1s)^2(\sigma_u 1s')^2$  where the prime indicates that the effective nuclear charge  $\zeta' = \zeta_u$  proper to the  $\sigma_u 1s'$  MO is in general different from  $\zeta = \zeta_g$  proper to the  $\sigma_g 1s$  MO. Thus, in the Huzinaga scheme, each  $\zeta$  value is

dependent on the MO to which it is assigned and also on the internuclear distance  $R$ . Accordingly, the wave function (1) determined in this fashion is called an "MO- $\zeta$ " wave function.<sup>9</sup> Huzinaga's energies at small distances are substantially lower than those of Griffing and Wehner<sup>3</sup> (G-W) who adopted a fixed value of  $\zeta_g = \zeta_u = 1.6875$  for all internuclear distances  $R$ . The reason for this improvement is that independent  $\zeta$  variation permits the  $g$  and  $u$  MO's to properly deform: The  $\sigma_g 1s$  MO tends to contract and the  $\sigma_u 1s'$  to expand as  $R$  gets smaller. The importance of independent MO deformation was also shown in similar computations on low-lying excited states of H<sub>2</sub>,<sup>10</sup> and a fuller discussion is to be found in the paper of Huzinaga.<sup>5b</sup>

While Huzinaga's energies are dramatically lower at

<sup>9</sup> R. S. Mulliken, *Revs. Modern Phys.* **32**, 232 (1960).

<sup>10</sup> P. E. Phillipson and R. S. Mulliken, *J. Chem. Phys.* **28**, 1248 (1958).

TABLE II. Comparison of single-ASOP energies with those deduced from experiments.  $\zeta_o$  and  $\zeta_u$  are determined to within  $\pm 0.01$  for  $R \leq 1.625$  Å; and within  $\pm 0.001$  for  $R > 1.625$  Å.

MO- $\zeta$ Parameters and $E_{o1}$ (in a.u.) <sup>a</sup>					$V(R)$ (in ev)			
$R$ (Å)	$R$ (a.u.)	$\zeta_o$	$\zeta_u$	$-E_{o1}$	MO- $\zeta$ <sup>a</sup>	G-W <sup>b</sup>	Ransil <sup>c</sup>	From experiment <sup>d</sup>
0	0	3.68	0.36	14.17872	$\infty$	$\infty$	$\infty$	
0.500	0.945180	2.23	0.99	8.87555	28.62	44.90	30.84	9.973
0.625	1.181474	2.04	1.22	8.41812	18.03	25.08		6.689
0.750	1.417769	1.92	1.38	8.10290	11.26	14.32	11.34	4.827
0.875	1.654064	1.84	1.49	7.85853	6.940			3.663
1.000	1.89036	1.79	1.57	7.65582	4.231	4.790	4.104	3.471
1.080	2.041588	1.77	1.60	7.54193	3.065			2.357
1.125	2.126654	1.75	1.62	7.48241	2.552			1.919
1.250	2.362949	1.73	1.65	7.33222	1.521	1.603	1.416	1.130
1.375	2.599244	1.71	1.67	7.20133	0.8951			0.6995
1.500	2.835538	1.70	1.68	7.08690	0.5190	0.5250	0.4557	0.4516
1.625	3.071834	1.69	1.69	6.98657	0.2964			0.2785
1.750	3.308129	1.687	1.693	6.89835	0.1660	0.1666	0.1321	0.1610
1.875	3.544423	1.684	1.695	6.82050	0.09118			0.08985
2.000	3.780718	1.683	1.695	6.75151	0.04898	0.05112	0.03224	0.04808
$\infty$	$\infty$	1.6875	1.6875	5.69531	0	0	0	0

<sup>a</sup> Present calculation.

<sup>b</sup> See reference 3. Energies recomputed in the present paper at the stated  $R$  values for comparative purposes.

<sup>c</sup> See reference 8.

<sup>d</sup> For  $0.5 \text{ Å} \leq R \leq 1.625 \text{ Å}$ ,  $V$  computed from equation 3; for  $R > 1.625 \text{ Å}$ ,  $V$  computed from the expression  $V(R) = (4/R)[1 + 0.265R - 2.419R^2 + 2.616R^3 - 0.436R^4] \exp(-2.48R)$  a.u. obtained by Buckingham by combining Amdur's 1949 and 1954 results (Eq. 3) with equilibrium and transport data on gaseous helium [R. A. Buckingham, Trans. Faraday Soc. 54, 453 (1958)].

small  $R$  values than the energies from previous computations, they are to be contrasted with the analysis of helium-helium scattering experiments by Amdur *et al.*,<sup>11</sup> who at various times reported the following expressions for the  $\text{He}_2$  potential in the ranges of internuclear distances indicated:

$$\begin{aligned}
 V(R) &= 2.884R^{-1.79} \text{ ev, } (0.52 \text{ Å} < R < 1.02 \text{ Å}) \text{ (1949)} \\
 &= 3.471R^{-5.03} \text{ ev, } (0.97 \text{ Å} < R < 1.48 \text{ Å}) \text{ (1961)} \text{ (3)} \\
 &= 4.713R^{-5.94} \text{ ev, } (1.27 \text{ Å} < R < 1.59 \text{ Å}) \text{ (1954).}
 \end{aligned}$$

A comparison of Huzinaga's energies with those of Amdur *et al.* (Table II) indicates a notable discrepancy between the calculated repulsion energies, especially at small internuclear distances, and those of Amdur. Huzinaga concluded that this discrepancy was due to the limitations inherent in his restriction to a single-configuration wave function, as well as the fact that his values of  $\zeta_o$  and  $\zeta_u$  were guessed and not determined by precise minimization.

The rather surprising disagreement between theoretical computations and the results deduced from scattering experiments for small internuclear distances has prompted the present more accurate series of computations on the  $^1\Sigma_g^+$  ground state of  $\text{He}_2$ . As a first step the single configuration procedure of Huzinaga was refined by accurate optimization of the variational parameters, for a larger number of  $R$  values. Details of the computation and results are presented in the next section.

The second step was to relax the restriction that the molecular wave function be represented by a single ASOP. In principle, an exact determination of the best

single ASOP of the form of Eq. (1) yields by definition the Hartree-Fock (self-consistent field) energy for the  $\text{He}_2$  molecule.<sup>12</sup> The difference between the Hartree-Fock energy (the lowest energy obtainable with a single ASOP) and the exact nonrelativistic energy is referred to as the correlation energy. To be more specific, the electronic motions are not really independent so that strictly it is improper to assign each electron to a private single-particle MO; on the contrary, the electrons tend to stay out of each other's way. In other words, their motions are correlated, and this correlation effect can be taken into account either by including interparticle electronic coordinates explicitly in the wave function,<sup>13</sup> or by expressing the wave function as a linear combination of configurations each similar in form to Eq. (1), that is, by superposition of configurations.<sup>14</sup> Accordingly, using the single-ASOP (single configuration) results of Sec. II as the point of departure, Sec. III will be devoted to superposition of configurations, with attention focused on the energetic effects of added configurations, as well as on an analysis of the relative importance of the configurations employed. The results of this study lead to the conclusion that the repulsion energies deduced from scattering experiments [Eq. (3)] in the region  $0.5 \text{ Å} \leq R \leq 1.0 \text{ Å}$  are irreconcilably too high, suggesting therefore a reinvestigation of the scattering analysis. A fuller discussion of the situation will be presented in the final section.

<sup>12</sup> C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951).

<sup>13</sup> H. James and A. Coolidge, J. Chem. Phys. 1, 825 (1933); W. Kolos and C. C. J. Roothaan, Revs. Modern Phys. 32, 205 (1960).

<sup>14</sup> An exhaustive superposition of configurations treatment of two-, three-, and four-electron atoms has been given by A. W. Weiss, Phys. Rev. 122, 1826 (1961).

<sup>11</sup> I. Amdur, J. Chem. Phys. 17, 844 (1949); I. Amdur, A. L. Harkness, *ibid.* 22, 664 (1954); I. Amdur, J. E. Jordan, and S. O. Colgate, *ibid.* 34, 1525 (1961).

TABLE III. Comparison of MO- $\zeta$  energies at large distances with those of experiment.  $\zeta_g$  and  $\zeta_u$  are determined to within  $\pm 0.001$  for  $R=2.25, 2.50$  A, and to within  $\pm 0.0001$  for  $R \geq 2.7$  A.

$R$ (A)	$R$ (a.u.)	$\zeta_g$	$\zeta_u$	$-\epsilon_g$ (a.u.)	$-\epsilon_u$ (a.u.)	$V(R)$ (ev)	$V(R)$ (from experiment) <sup>a</sup>
2.25	4.253308	1.682	1.694	0.90731	0.88513	$1.307 \times 10^{-2}$	$1.139 \times 10^{-2}$
2.50	4.725898	1.683	1.693	0.90219	0.89045	$3.035 \times 10^{-3}$	$1.284 \times 10^{-3}$
2.70	5.103970	1.6838	1.6914	0.89996	0.89296	$7.966 \times 10^{-4}$	$-5.917 \times 10^{-4}$
2.90	5.482042	1.6848	1.6903	0.89855	0.89440	$1.455 \times 10^{-4}$	$-8.174 \times 10^{-4}$
3.10	5.860113	1.6856	1.6895	0.89769	0.89525	$-9.25 \times 10^{-6}$	$-6.185 \times 10^{-4}$
3.30	6.238185	1.6862	1.6888	0.89720	0.89577	$-2.846 \times 10^{-5}$	$-3.890 \times 10^{-4}$
3.50	6.616257	1.6866	1.6884	0.89690	0.89607	$-2.000 \times 10^{-5}$	$-2.227 \times 10^{-4}$
4.00	7.561437	1.6872	1.6878	0.89659	0.89638	$-3.54 \times 10^{-6}$	$-4.287 \times 10^{-5}$
$\infty$		1.6875	1.6875	0.89648	0.89648	0	0

<sup>a</sup> Computed from Buckingham curve (reference d, Table II).

## II. SINGLE CONFIGURATION TREATMENT

The electronic Hamiltonian for He<sub>2</sub> in atomic units<sup>15</sup> is given by

$$\mathcal{H} = \sum_{i=1}^2 H(i) + \sum_{i>j=1}^2 \frac{1}{r_{ij}}, \quad (4)$$

where

$$H(i) = -\frac{1}{2}\nabla_i^2 - 2/r_{ai} - 2/r_{bi}. \quad (5)$$

The lowest eigenvalue of (4) is the ground-state electronic energy  $E_{el}(R)$ , where  $R$  is the internuclear distance between nuclei  $a$  and  $b$ . The intermolecular repulsive potential  $V(R)$  is related to  $E_{el}(R)$  by

$$V(R) = E_{el}(R) + 4/R - 2E(\text{He}) = E_T(R) - 2E(\text{He}), \quad (6)$$

$E_T$  is the total molecular energy, and  $2E(\text{He})$  represents the energy of two <sup>1</sup>S ground-state helium atoms. Using the single ASOP wave function of Eq. (1), the electronic energy is given by

$$\begin{aligned} E_{el} &= \int \Psi_{\text{MOQ}} \mathcal{H} \Psi_{\text{MO}} dV \\ &= 2H_g + 2H_u + J_{gg} + J_{uu} + 4J_{gu} - 2K_{gu}, \end{aligned} \quad (7)$$

where

$$\begin{aligned} H_g &= \int 1\sigma_g(1)H(1)1\sigma_g(1)dV_1, \\ H_u &= \int 1\sigma_u(1)H(1)1\sigma_u(1)dV_1, \\ J_{gg} &= \iint 1\sigma_g(1)1\sigma_g(1)\left(\frac{1}{r_{12}}\right)1\sigma_g(2)1\sigma_g(2)dV_1dV_2, \\ J_{uu} &= \iint 1\sigma_u(1)1\sigma_u(1)\left(\frac{1}{r_{12}}\right)1\sigma_u(2)1\sigma_u(2)dV_1dV_2, \\ J_{gu} &= \iint 1\sigma_g(1)1\sigma_g(1)\left(\frac{1}{r_{12}}\right)1\sigma_u(2)1\sigma_u(2)dV_1dV_2, \\ K_{gu} &= \iint 1\sigma_g(1)1\sigma_u(1)\left(\frac{1}{r_{12}}\right)1\sigma_g(2)1\sigma_u(2)dV_1dV_2. \end{aligned} \quad (8)$$

The one-electron, or orbital, energies are then given by<sup>12</sup>

$$\begin{aligned} \epsilon_g &= H_g + J_{gg} + 2J_{gu} - K_{gu}, \\ \epsilon_u &= H_u + J_{uu} + 2J_{gu} - K_{gu}. \end{aligned} \quad (9)$$

TABLE IV. Orbital energies (in a.u.).

$R$ (A)	MO- $\zeta$ (Present calculation)		G-W		Ransil	
	$-\epsilon_g$	$-\epsilon_u$	$-\epsilon_g$	$-\epsilon_u$	$-\epsilon_g$	$-\epsilon_u$
0	4.94837	0.16556				
0.500	1.90918	0.30071	1.52865	0.06525	1.77831	0.21882
0.625	1.55353	0.39917				
0.750	1.34201	0.50275	1.25545	0.45903	1.32552	0.48415
0.875	1.20812	0.59255				
1.000	1.11725	0.66315	1.09986	0.65704	1.11950	0.65945
1.080	1.07602	0.70082				
1.125	1.05685	0.72027				
1.250	1.01376	0.76343	1.01204	0.76418	1.01785	0.76291
1.375	0.98355	0.79738				
1.500	0.96134	0.82289	0.96192	0.82378	0.96391	0.82225
1.625	0.94474	0.84203				
1.750	0.93232	0.85625	0.93311	0.85697	0.93412	0.85586
1.875	0.92312	0.86695				
2.000	0.91624	0.87489	0.91666	0.87526	0.91734	0.87461
$\infty$	0.89648	0.89648	0.89648	0.89648	0.89648	0.89648

<sup>15</sup> The following units are used throughout this paper: energy units are 1 a.u. = 27.210 eV, length units are 1 a.u. = 0.5290 A.

TABLE V. He<sub>2</sub> separated atom energies and united atom energies.

He <sub>2</sub> Separated atom energies [ $2E(\text{He})$ ]			He <sub>2</sub> united atom energies		
He atom wave function	Energy (in a.u.)	Diff. from H.F. (in ev)	Be atom wave function	Energy (in a.u.)	Diff. from H.F. (in ev)
1s <sup>2</sup> (MO- $\zeta$ )	-5.69531	+0.763	1s <sup>2</sup> 1p <sup>2</sup> (MO- $\zeta$ )	-14.179	+10.72
Hartree-Fock <sup>a</sup>	-5.72336	0	1s <sup>2</sup> 2p <sup>2</sup> (exp.) <sup>b</sup>	-14.387	+5.06
$\Psi_{10}(1s, 1s')$ <sup>b</sup>	-5.740	-0.453	1s <sup>2</sup> 1s' <sup>2</sup> f	-14.506	+1.82
1s1s' <sup>c</sup>	-5.75132	-0.761	1s <sup>2</sup> 2s <sup>2</sup> f	-14.557	+0.435
$\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$ <sup>b</sup>	-5.755	-0.861	Hartree-Fock <sup>a</sup>	-14.573	0
1s1s'+ $\lambda$ 2p <sup>2</sup> <sup>c</sup>	-5.79046	-1.83	1s1s'2s <sup>2</sup> f	-14.580	-0.190
Exact <sup>d</sup>	-5.80744	-2.29	1s <sup>2</sup> 2s <sup>2</sup> (exact) <sup>g</sup>	-14.667	-2.56

<sup>a</sup> C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Revs. Modern Phys. **32**, 186 (1960).

<sup>b</sup> The superposition of configuration SAE's could be determined only to three decimal figures, since at large internuclear distances various configurations become linearly dependent due to the loss of the  $g$  and  $u$  symmetry distinction. This resulted in loss of significant figures. The stated separation energies are extrapolations based primarily on the computations performed at 2.0 Å.

<sup>c</sup> J. N. Silverman, O. Platas, and F. A. Matsen, J. Chem. Phys. **32**, 1402 (1960).

<sup>d</sup> C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959).

<sup>e</sup> This energy represents  $\frac{1}{3}1s1s'2p^2 + \frac{2}{3}1s1s'2s^2$  where  $1s1s'2p^2$  and  $1s1s'2s^2$  are the experimental values 71 498.9 cm<sup>-1</sup> and 56 432.5 cm<sup>-1</sup>, respectively, above 1s<sup>2</sup>2s<sup>2</sup>1S ground state of Be [*Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1948), Vol. 1].

<sup>f</sup> G. H. Brigrman, R. P. Hurst, J. P. Gray, and F. A. Matsen, J. Chem. Phys. **29**, 251 (1958).

<sup>g</sup> See reference 14.

Following the procedure of Huzinaga, the MO's of Eq. (2) were used so that the electronic energy becomes parametrically a function of  $\zeta_g$  and  $\zeta_u$ . The procedure was simply to determine at a given  $R$  value the  $\zeta_g$ - $\zeta_u$  pair which minimizes the energy. The computed energies for  $R \leq 2.0$  Å are shown in Table II under the heading "MO- $\zeta$ ", for  $R > 2.0$  Å in Table III, and the electronic energy curve is shown in Fig. 1 (curve A); the orbital energies are given in Table IV. The most salient feature is the large lowering of the repulsion energy at small distances over that of G-W,<sup>3</sup> for which  $\zeta_g = \zeta_u = 1.6875$  for all  $R$ . In particular, at 0.5 Å the MO- $\zeta$  repulsion energy is more than 16 ev lower than G-W, which emphasizes the extreme importance of permitting independent molecular orbital deformation. Furthermore, a comparison of the MO- $\zeta$  repulsion energies with those computed from Huzinaga's values of  $a=234$  and  $b=4.09$  (Table I) shows good agreement, and indicates that his estimated  $\zeta_g$  and  $\zeta_u$  values are not far from the best values as determined here.

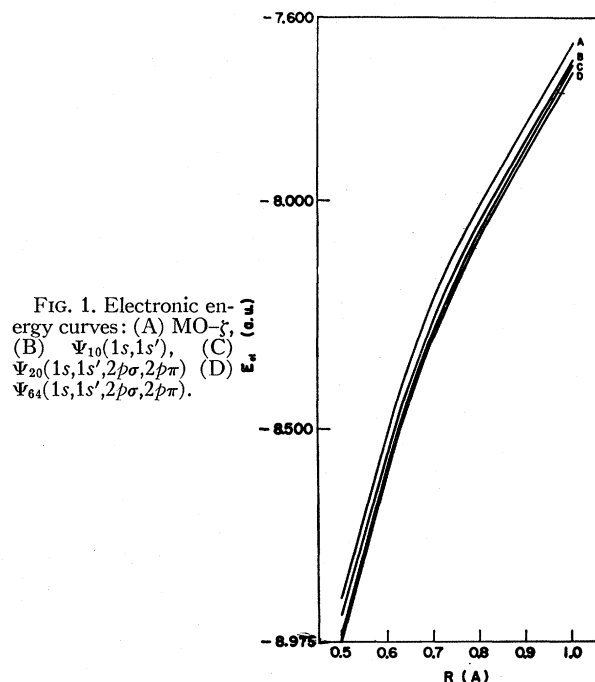
However, from a united atom point of view, the limitations of the single-ASOP representation of Eq. (1) are particularly apparent. First of all, as  $R \rightarrow 0$ , the  $(1\sigma_g)^2(1\sigma_u)^2$  configuration [see Eq. (1)] goes into a  $1s^22p^2$  excited state of Be composed of a mixture of one-third  $1s^22p^2^1S$  and two-thirds  $1s^22p^2^1D$ .<sup>16</sup> This state formally lies 7.62 ev above the  $1s^22s^2^1S$  exact ground state of Be which is the proper united atom limit of the  $^1\Sigma_g^+$  state of the He<sub>2</sub> molecule (see Table V). Furthermore, with the approximation  $1\sigma_u = \sigma_u 1s'$  [see Eq. (2)] the  $\sigma_u 1s'$  MO goes over into what may be called a "1p $\sigma$ " AO. That is,

$$\lim_{R \rightarrow 0} \sigma_u 1s' = 1p\sigma = (3\zeta'^{1/3}/\pi)^{1/2} e^{-\zeta' r} \cos\theta. \quad (10)$$

While this function has the same nodal behavior as a

<sup>16</sup> C. C. J. Roothaan, Laboratory of Molecular Structure and Spectra, University of Chicago Technical Report, 1955 (unpublished), p. 24.

$2p\sigma$  AO, the absence of the proper radial factor present in a legitimate  $2p\sigma$  AO results in non-single-valuedness of this functional form at  $R=0$ . A separate computation of the  $1s^21p^2$  ( $\frac{1}{3}^1S + \frac{2}{3}^1D$ ) of Be leads to an electronic energy of -14.179 a.u., which is 5.66 ev above the value of  $1s^22p^2$  ( $\frac{1}{3}^1S + \frac{2}{3}^1D$ ) obtained using experimental  $^1S$  and  $^1D$  energies, and 13.28 ev above the  $1s^22s^2^1S$  exact ground-state energy (Table V). Similarly, inspection of Table V indicates that the energy  $2E(\text{He})$  of two separated He atoms is 3.05 ev above the exact value. This suggests that the intermolecular potential, which is the difference between the total energy and the separated atoms energy (SAE) is in error by no more than a maximum of 10 ev. Furthermore, it is reasonable



to assume that the error increases rapidly as  $R$  gets smaller, so that for distances greater than 0.5 Å, the error in the repulsion energy should not exceed 5 eV. These conclusions appear to contradict the scattering results; for example, the remaining discrepancy between the MO- $\zeta$  repulsion energy and that obtained from scattering at 0.5 Å is approximately 18 eV.

A comparison of the MO- $\zeta$  energies with those of Ransil is of interest. Ransil's calculation was of an extended LCAO-MO-SCF type, the  $1\sigma_g$  and  $1\sigma_u$  MO's being expressed as linear combinations of  $1s$ ,  $2s$ , and  $2p\sigma$  STO's. In principle, the construction of the  $1\sigma_g$  and  $1\sigma_u$  MO's out of a complete STO basis set should yield the best Hartree-Fock (self-consistent field) energy, that is, the best energy obtainable from a single ASOP. However, Ransil's basis set was limited to the above STO's and his nonlinear parameter variation was restricted to finding the best  $\zeta$  common to all STO's ( $\zeta_{1s}=\zeta_{2s}=\zeta_{2p\sigma}$ ) and common to both the  $1\sigma_g$  and  $1\sigma_u$  MO's ( $\zeta_g=\zeta_u$ ) for each  $R$  value. Thus, Ransil's repulsion energies for small  $R$  values ( $R \leq 0.75$  Å) are not as low as the MO- $\zeta$  energies, the latter obtained using a wave function which incorporates the important feature of independent orbital  $\zeta$  variation. However, at distances greater than 0.75 Å, Ransil's energies are lower, since here  $\zeta_g \sim \zeta_u$  and the independent MO- $\zeta$  variation has less effect, while Ransil's function has the advantage of including  $2s$  and  $2p\sigma$  in the STO basis set.

It is to be emphasized that both Ransil's energies and the MO- $\zeta$  energies are higher than the lowest energy obtainable from the single ASOP, that is, the true Hartree-Fock energy. This is most easily seen upon consideration of the fact that both the MO- $\zeta$  and Ransil's reported SAE is  $-5.69531$  a.u. which is 0.76 eV higher than the Hartree-Fock energy of two helium atoms (Table V). As distinct from most diatomic molecules, the separated helium atoms as well as the  $\text{He}_2$  molecule are closed shell systems in the ground state. Hence, if the MO's  $1\sigma_g$  and  $1\sigma_u$  are expressed as the sum and difference of STO's as in Eq. (2), then the unnormalized wave function

$$\Psi_{\text{VB}} = (4!)^{-1/2} |a(1)\alpha(1)a(2)\beta(2)b(3)\alpha(3)b(4)\beta(4)|, \quad (11)$$

is the valence-bond function equivalent to  $\Psi_{\text{MO}}$  [Eq. (1)]. In other words,  $\Psi_{\text{MO}}$  and  $\Psi_{\text{VB}}$  differ only by a normalization factor which depends upon the internuclear distance, so that energetically they yield the same results. At  $R = \infty$ , then, the Hartree-Fock  $\text{He}_2$  molecule ASOP should exactly dissociate into two Hartree-Fock helium atoms. This is to be contrasted with, for example, the ground state of  $\text{H}_2$  in which the MO and Heitler-London (VB) methods yield different results.<sup>17</sup> In the refinements to be considered in the next section, further attention will be paid to the asymptotic energies computed at infinity (the SAE) and for the

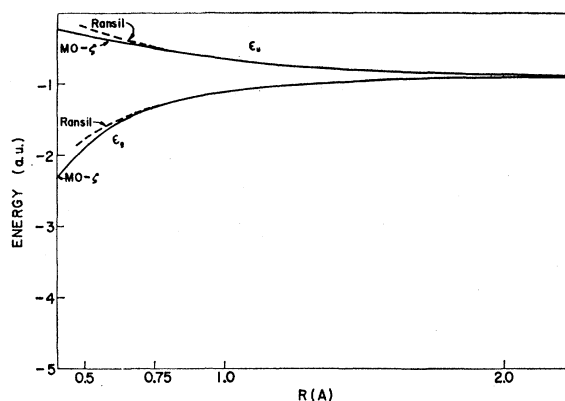


FIG. 2. Orbital energy curves.

united atom as an index of the accuracy of the wave function at finite internuclear distances.

A comparison of the orbital energies (Table IV and Fig. 2) is of some interest. In particular it will be noticed that the G-W orbital energies are higher than the MO- $\zeta$  orbital energies for  $R \leq 1.0$  Å but are lower for  $R \geq 1.5$  Å; at 1.25 Å  $\epsilon_g$  is higher but  $\epsilon_u$  is lower. The  $\epsilon_g$ 's of Ransil at 0.5 and 0.75 Å are higher than the MO- $\zeta$   $\epsilon_g$ 's but lower at all larger distances. This is exactly parallel to the relative behaviors of the repulsion energy. However, at all distances the Ransil  $\epsilon_u$ 's are higher than the corresponding MO- $\zeta$   $\epsilon_u$ 's. These varied results illustrate that the  $\epsilon$ 's have a sensitive dependence to the approximations used for the MO's when they are not exact Hartree-Fock solutions, but the nature of this dependence is not clear.

While this study is primarily concerned with the repulsion energy between two ground-state helium atoms, it might be mentioned that at large distances the MO- $\zeta$  function  $(\sigma_g 1s)^2 (\sigma_u 1s')^2$  is good enough to give some indication of the van der Waals attraction energy. Inspection of Table III shows first of all that at large distances  $\zeta_g$  falls slightly below  $\zeta_u$  in contrast to its behavior at shorter distances where  $\zeta_g > \zeta_u$ . This results in a contraction of the  $\sigma_u 1s'$  MO with a consequent polarization effect, and illustrates that  $\sigma_u 1s'$  even at large distances is capable of exhibiting the qualitative behavior one would expect of a  $\sigma_u 2p$  MO. That the computed repulsion energy did not become negative when the free atom  $\zeta_g = \zeta_u = 1.6875$  was used again emphasizes the importance of  $\zeta$  variation. However, the energy minimum was computed to be at 3.3 Å as compared to the reported experimental distance of 2.9 Å. Furthermore, the magnitude of the computed attraction energy is but a few percent of that deduced from experiment. Nevertheless, that an energy minimum is observed at all as a result of this variational calculation is of interest.<sup>18</sup>

<sup>17</sup> For a further discussion of these points, see J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Company, Inc., New York, 1951), pp. 225-227.

<sup>18</sup> For the latest discussion of the He+He van der Waals energy, see reference 7 and also N. Lynn, *Proc. Phys. Soc. (London)* **72**, 201 (1958).

TABLE VI. Superposition of configurations—electronic and total energies (in a.u.). The three numbers in each set are in order,  $E_{el}$ ,  $E_T$ , and improvement over MO- $\zeta$  (in ev.)

Wave function	No. of config.	Energies				
		0.5 A	0.625 A	0.75 A	1.0 A	2.0 A
MO- $\zeta$	1	-8.87555 -4.64355	-8.41812 -5.03252	-8.10290 -5.28157	-7.65582 -5.53982	-6.75151 -5.69351
$\Psi_{10}(1s, 1s')$	10	-8.91513 -4.68313 (1.077)	-8.46172 -5.07612 (1.186)	-8.14400 -5.32267 (1.118)	-7.69443 -5.57843 (1.051)	-6.79529 -5.73729 (1.191)
$\Psi_{17}(1s, 1s', 2p\sigma)$	17	-8.94817 -4.71617 (1.976)	-8.48417 -5.09857 (1.797)	-8.15945 -5.33812 (1.539)	-7.70273 -5.58673 (1.276)	-6.79713 -5.73913 (1.241)
$\Psi_{39}(1s, 1s', 2p\sigma)$	39	-8.95402 -4.72202 (2.135)	-8.49037 -5.10477 (1.966)	-8.16659 -5.34526 (1.733)	-7.70925 -5.59325 (1.454)	-6.80101 -5.74301 (1.347)
$\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$	20	-8.95744 -4.72544 (2.228)	-8.49212 -5.10652 (2.014)	-8.16625 -5.34492 (1.724)	-7.70781 -5.59181 (1.415)	-6.80024 -5.74224 (1.326)
$\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$	64	-8.96695 -4.73495 (2.487)	-8.50386 -5.11826 (2.333)	-8.18023 -5.35890 (2.104)	-7.72183 -5.60583 (1.796)	-6.81179 -5.75379 (1.640)

### III. SUPERPOSITION OF CONFIGURATIONS TREATMENT

The preceding discussion of the practical and theoretical limitations of the single-ASOP approximation emphasizes the desirability of improving the molecular wave function by the method of superposition of configurations (commonly called configuration interaction). Formally, this means that the wave function is expressed as a linear combination of  $1\Sigma_g^+$  wave functions each corresponding to a different electron configuration. The  $\text{He}_2$  molecular wave function is then expressed as

$$\Psi_n = \sum_{i,j,k} c_{ijk} D_{ijk}, \quad (12)$$

where  $D_{ijk}$  refers to a given configuration and is a linear combination of in general four ASOP's:

$$\begin{aligned} D_{ijk} = N_{ijk} [ & |\phi_i^*(1)\alpha(1)\phi_i(2)\beta(2)\phi_j^*(3)\alpha(3)\phi_k(4)\beta(4)| \\ & + |\phi_i^*(1)\alpha(1)\phi_i(2)\beta(2)\phi_k^*(3)\alpha(3)\phi_j(4)\beta(4)| \\ & + |\phi_i^*(1)\alpha(1)\phi_i(2)\beta(2)\phi_j(3)\alpha(3)\phi_k^*(4)\beta(4)| \\ & + |\phi_i^*(1)\alpha(1)\phi_i(2)\beta(2)\phi_k(3)\alpha(3)\phi_j^*(4)\beta(4)| ] \\ \equiv & (\phi_i)^2(\phi_j\phi_k). \end{aligned} \quad (13)$$

The asterisks indicate complex conjugate, and  $N_{ijk}$  is the appropriate normalization factor such that each configuration  $D_{ijk}$  is normalized to one. The superscript in  $\Psi_n$  denotes the number of configurations, and the coefficients  $c_{ijk}$  are determined by the condition that the electronic energy be an extremum, leading to the eigenvalue equation

$$\begin{aligned} \sum_{\lambda} H_{\lambda u} c_{\lambda u} &= E_{el} \sum_{\lambda} S_{\lambda u} c_{\lambda u}, \\ H_{\lambda u} &= \int D_{\lambda}^* \mathcal{H} D_u dV, \\ S_{\lambda u} &= \int D_{\lambda}^* D_u dV, \quad S_{\lambda\lambda} = 1, \end{aligned} \quad (14)$$

where  $\lambda$  and  $u$  refer collectively to  $(ijk)$ . The molecular orbitals  $\varphi$  are expressed as the sum or difference of normalized STO's  $\chi_{nlm}$  centered around nuclei  $a$  and  $b$ :

$$\begin{aligned} \chi_{nlm} &= (2n!)^{-\frac{1}{2}} (2\zeta_{nl})^{n+\frac{1}{2}} r^{n-1} \exp(-\zeta_{nl}r) Y_{lm}(\theta, \varphi); \\ n=1, \quad l=m=0, & \quad 1s\sigma \\ n=2, \quad l=m=0, & \quad 2s\sigma \\ n=2, \quad l=1, \quad m=0, & \quad 2p\sigma \\ n=2, \quad l=1, \quad m=\pm 1, & \quad 2p\pi, 2p\bar{\pi}. \end{aligned} \quad (15)$$

It is important to note that the configurations are basically of two types: those  $D_{ijk}$ 's for which  $j=k$  represent configurations in which two MO's  $i$  and  $j$  are doubly occupied; and those  $D_{ijk}$ 's for which  $j \neq k$  represent configurations in which the  $i$ th MO is doubly occupied and the  $j$ th and  $k$ th MO's are singly occupied. Limitations of the machine program prevented the inclusion of configurations in which all four electrons are in distinct singly-occupied MO's. That is, configurations of the form  $(\phi_i\phi_j\phi_k\phi_l)$  have been excluded. The effect of this neglect will be discussed below.

### Ten-Configuration Treatment using 1s STO's Only

A direct generalization of the MO- $\zeta$  treatment is to relax the condition that  $\zeta_{1s}$  ( $\zeta_a$ ) be confined to the  $\sigma_a 1s$  MO and  $\zeta_{1s'}$  ( $\zeta_u$ ) be confined to the  $\sigma_u 1s'$  MO and consider all configurations built from the molecular orbitals

$$\begin{aligned} \sigma_a 1s &= N_a [1s_a + 1s_b], & \sigma_u 1s &= N_u [1s_a - 1s_b], \\ \sigma_a 1s' &= N_a' [1s_a' + 1s_b'], & \sigma_u 1s' &= N_u' [1s_a' - 1s_b']. \end{aligned} \quad (16)$$

The ten possible independent configurations of the form of Eq. (13) are given in Table VII which includes the values of  $\zeta_{1s}$ ,  $\zeta_{1s'}$  and the coefficients at the five internuclear distances at which computations were

TABLE VII. Coefficients, parameters, and energies for  $\Psi_{10}(1s, 1s')$ . At each  $R$ ,  $\zeta_{1s}$  and  $\zeta_{1s'}$  were independently varied in steps of 0.05 over a two-dimensional  $\zeta_{1s}-\zeta_{1s'}$  grid until the energy passed through a minimum. The  $\zeta$  pairs reported here were then determined by graphical interpolation.

Configurations	Coefficients				
	0.5 A	0.625 A	0.75 A	1.0 A	2.0 A
1. $(\sigma_g 1s)^2(\sigma_u 1s')^2$	+0.74057	+0.45873	+0.23932	+0.02786	-0.03005
2. $(\sigma_g 1s')^2(\sigma_u 1s)^2$	-0.02025	-0.03684	-0.05495	-0.08187	-0.02918
3. $(\sigma_g 1s)^2(\sigma_g 1s')^2$	-0.05786	-0.03461	-0.03125	-0.03519	-0.03261
4. $(\sigma_u 1s)^2(\sigma_u 1s')^2$	-0.03728	-0.03206	-0.02774	-0.02197	-0.02306
5. $(\sigma_g 1s)^2(\sigma_u 1s)^2$	-0.14797	-0.06571	-0.23134	-0.22900	-0.13488
6. $(\sigma_g 1s')^2(\sigma_u 1s')^2$	-0.05133	-0.06588	-0.09440	-0.20536	-0.10645
7. $(\sigma_g 1s)^2(\sigma_u 1s\sigma_u 1s')$	+0.35104	+0.61953	+0.71152	+0.37908	+0.17840
8. $(\sigma_u 1s)^2(\sigma_g 1s\sigma_g 1s')$	+0.08732	+0.17409	+0.27115	+0.25327	+0.16800
9. $(\sigma_g 1s')^2(\sigma_u 1s\sigma_u 1s')$	+0.04714	+0.05626	+0.09226	+0.41692	+0.50435
10. $(\sigma_u 1s')^2(\sigma_g 1s\sigma_g 1s')$	+0.00419	+0.01809	+0.08726	+0.46386	+0.48183
Parameters and energies					
$\zeta_{1s}$	2.25	2.10	2.05	2.25	2.39
$\zeta_{1s'}$	0.84	0.92	0.99	1.24	1.33
$V(R)$ (ev) <sup>a</sup>	28.76	18.06	11.36	4.396	0.074

<sup>a</sup> Separation energy taken to be -5.740 a.u. (Table V).

made. The energies are given in Table VI under the designation  $\Psi_{10}(1s, 1s')$  and the electronic energy curve in Fig. 1 (curve B). The most notable result is that the lowering of the electronic energy over that of the single MO- $\zeta$  configuration is remarkably constant, it being  $1.1 \pm 0.1$  ev over the range of  $R$  considered (Table VI). Thus, the effect of superposition of configurations in this case is to depress the electronic curve uniformly. Since the repulsion energy is essentially the difference between the electronic energy and the SAE, the energy improvements cancel. The net result is that the *repulsion energies* are approximately *unchanged* over those of the MO- $\zeta$  approximation, as a comparison of the  $V(R)$  values in Table VII with the corresponding MO- $\zeta$  values in Table II indicates.

It should be noted that the neglect of the configuration  $(\sigma_g 1s\sigma_g 1s'\sigma_u 1s\sigma_u 1s')$ , in which all electrons are in distinct singly-occupied MO's affects particularly the SAE. The inclusion of this (eleventh) configuration would guarantee that the wave function would dissociate exactly into the product of two helium-atom wavefunctions each of the form  $1s(1)1s'(2) + 1s(2)1s'(1)$ . The helium-atom pair  $^1S(1s1s') + ^1S(1s1s')$  gives an energy which is 0.761 ev below the Hartree-Fock (see Table V), while  $\Psi_{10}(1s, 1s')$  yields an SAE 0.308 ev higher than this value, yet 0.453 ev below the Hartree-Fock value and 1.216 ev lower than the MO- $\zeta$  SAE. That the effect of this neglect is most serious at large internuclear separations can be seen by a study of the coefficients in Table VII. At 0.5 A  $(\sigma_g 1s)^2(\sigma_u 1s')^2$  has the largest coefficient, while  $(\sigma_g 1s)^2(\sigma_u 1s\sigma_u 1s')$  and  $(\sigma_g 1s')^2(\sigma_u 1s)^2$  have the two next largest; at 0.625 A  $(\sigma_g 1s)^2(\sigma_u 1s\sigma_u 1s')$  and  $(\sigma_g 1s')^2(\sigma_u 1s')^2$  exchange roles in importance and the configuration  $(\sigma_u 1s)^2(\sigma_g 1s\sigma_g 1s')$  replaces  $(\sigma_g 1s)^2(\sigma_u 1s)^2$ . At 1.0 A and 2.0 A it is seen that all the largest coefficients are associated with configurations 7 through 10 in which two electrons are in singly occupied MO's. Therefore, it is reasonable to suppose that the importance of the missing  $(\sigma_g 1s\sigma_g 1s'\sigma_u 1s\sigma_u 1s')$  configuration increases with increasing  $R$ , and its neglect affects

most seriously the SAE, but only negligibly the energy at finite  $R$ .

As for the united atom, it is seen that even at 0.5 A the  $(\sigma_g 1s)^2(\sigma_g 1s')^2$  configuration is not very important (its coefficient being small) although at some distance less than 0.5 A it must take precedence over the  $(\sigma_g 1s)^2(\sigma_u 1s')^2$  configuration.<sup>19</sup> At the united atom limit,  $(\sigma_g 1s)^2(\sigma_g 1s')^2$  goes over into  $1s^2 1s'^2$  yielding an energy 8.9 ev lower than the MO- $\zeta$  united atom energy, only 1.82 ev higher than the Hartree-Fock, and 4.38 ev higher than the exact  $1s^2 2s^2$  ground-state energy.

It is concluded, then, that  $\Psi_{10}(1s, 1s')$  gives an SAE 1.84 ev too high, although this SAE is lower than for the Hartree-Fock approximation, and that the united atom energy is certainly no more than 4.38 ev above the exact Be ground state. These energy differences in the SAE and united atom energy are to be compared with the corresponding values of 3.05 and 13.28 ev yielded by the MO- $\zeta$  wave function discussed in the previous section.

[It is interesting in this connection to relate  $\Psi_{10}(1s, 1s')$  with the valence-bond treatment of Rosen,<sup>2</sup> which presumably was a refinement of Slater's earlier calculation.<sup>1</sup> Just as  $\Psi_{10}(1s, 1s')$  is an extension of the single ASOP MO wave function of Eq. (1), so Rosen's calculation was an extension of the equivalent valence-bond function of Eq. (2). In general, one can form six singlet ASOP's out of the AO's  $1s_a, 1s_a', 1s_b, 1s_b'$ . (See Eyring, Walter, and Kimball.<sup>20</sup>) Rosen took a particular linear combination of four of them to form a "bond eigenfunction"  $\Psi_1(a-a'; b-b')$  corresponding to a "bond" between the

<sup>19</sup> The configuration  $(\sigma_g 1s)^2(\sigma_g 1s')^2$  is an approximate representation of  $(\sigma_g 1s)^2(\sigma_g 2s)^2$  since the  $2s$  STO can be fairly well represented by  $(1-\lambda^2)^{-1/2}(1s' - \lambda 1s)$ , where  $\lambda$  is the overlap integral of  $1s$  and  $1s'$ . While  $(1\sigma_g)^2(1\sigma_u)^2 \sim (\sigma_g 1s)^2(\sigma_u 1s')^2$  correctly describes the  $\text{He}_2$  molecule at finite  $R$ , as the united atom is approached, the configuration  $(1\sigma_g)^2(2\sigma_g)^2 \sim (\sigma_g 1s)^2(\sigma_g 2s)^2$  should have lower energy, since the latter configuration goes properly into  $1s^2 2s^2$  of Be as  $R \rightarrow 0$ . The results discussed here indicate that even at 0.5 A the united atom configuration  $(\sigma_g 1s)^2(\sigma_g 1s')^2$  energetically lies well above  $(\sigma_g 1s)^2(\sigma_u 1s')^2$ .

<sup>20</sup> H. Eyring, J. Walter, and G. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), Chap. XIII.



two electrons on center  $a$  and a second "bond" between two electrons on center  $b$ . However, he neglected higher "resonance structures" of the form  $\Psi_2(a-b; a'-b')$  and  $\Psi_3(a-b'; a'-b)$ . While these structures make no contribution to the SAE, they should become important for finite  $R$ ; in fact, at the united atom,  $\Psi_1 = \Psi_3$ . Consequently, Rosen's computed repulsion energies at small distances are very high (see Table I).]

### Extended Treatment Including Two-Quantum STO's

The next stage of refinement was to include two-quantum STO's in the basis set. Configurations constructed of the following MO's were introduced into the wave function

$$\begin{aligned}\sigma_g 2s &= N_g^{2s} [2s_a + 2s_b], \\ \sigma_g 2p &= N_g^{2p\sigma} [2p\sigma_a + 2p\sigma_b], \\ \pi_g 2p &= N_g^{2p\pi} [2p\pi_a - 2p\pi_b], \\ \sigma_u 2s &= N_u^{2s} [2s_a - 2s_b], \\ \sigma_u 2p &= N_u^{2p\sigma} [2p\sigma_a - 2p\sigma_b], \\ \pi_u 2p &= N_u^{2p\pi} [2p\pi_a + 2p\pi_b].\end{aligned}\quad (17)$$

At first, 29 configurations involving  $\sigma_g 2s$  and  $\sigma_u 2s$  were added to the original  $\Psi_{10}(1s, 1s')$ . This 39 configuration wave function would insure a united atom energy at least as good as that for  $1s1s'2s^2$ , which gives a Be energy lower than the Hartree-Fock (Table V). However, computations at 0.5 Å (where in particular  $\sigma_g 2s$  would be expected to be important) revealed a negligible lowering of the electronic energy over  $\Psi_{10}(1s, 1s')$ : the energy improvement was 0.305 eV for an optimized  $\zeta_{2s}$  value of 2.0. This result indicates that the use of  $1s$  and  $1s'$  with optimized parameters  $\zeta_{1s}$  and  $\zeta_{1s'}$  accounts for most of the  $s$ -electron contribution and that a more decided improvement would be obtained by putting  $p$ -electron character into the molecular wave function.

Accordingly, further computations involving  $2s$  were abandoned, and the  $\sigma_g 2s$  and  $\sigma_u 2s$  MO's were replaced by  $\sigma_g 2p$  and  $\sigma_u 2p$ , giving a 39-configuration wave function (configurations 1-39 in the Appendix) denoted by  $\Psi_{39}(1s, 1s', 2p\sigma)$  in Table VI. By trial and error, it was found that of the 29 configurations containing  $2p\sigma$  added to  $\Psi_{10}(1s, 1s')$ , 7 contributed most significantly to the lowering of the electronic energy. The orbital exponent  $\zeta_{2p\sigma}$  common to  $\sigma_g 2p$  and  $\sigma_u 2p$  was varied in steps of 0.1 (with  $\zeta_{1s}$  and  $\zeta_{1s'}$  kept at their values which were best for  $\Psi_{10}(1s, 1s')$ ) to minimize the energy for these selected 17 configurations—configurations 1-17 in the Appendix—and denoted by  $\Psi_{17}(1s, 1s', 2p\sigma)$  in Table VI.<sup>21</sup>

<sup>21</sup> The value of  $\zeta_{2p\sigma}$  which minimized the energy for  $\Psi_{17}(1s, 1s', 2p\sigma)$  was always 0.2 or 0.3 larger than the  $\zeta_{2p\sigma}$  which minimized the energy for  $\Psi_{39}(1s, 1s', 2p\sigma)$ . The  $\Psi_{39}(1s, 1s', 2p\sigma)$  energy at  $\zeta_{2p\sigma}$  which minimized  $\Psi_{17}(1s, 1s', 2p\sigma)$  was never more than 0.01 eV higher than the  $\Psi_{39}(1s, 1s', 2p\sigma)$  energy at the smaller  $\zeta_{2p\sigma}$  optimized for  $\Psi_{39}(1s, 1s', 2p\sigma)$ . Thus, the electronic energies reported in Table VI are for  $\zeta_{2p\sigma}$  values which, strictly speaking, are the best for  $\Psi_{17}(1s, 1s', 2p\sigma)$ , but also minimize the 39 configuration energy within 0.01 eV.

The last step was the addition of 25 configurations involving  $\pi_g 2p$  and  $\pi_u 2p$  MO's to  $\Psi_{39}(1s, 1s', 2p\sigma, 2p\pi)$  to produce a 64-configuration wave function denoted by  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  in Table VI. Upon variation of  $\zeta_{2p\pi}$  common to  $\pi_g 2p$  and  $\pi_u 2p$  in steps of 0.2 [with  $\zeta_{1s}$ ,  $\zeta_{1s'}$ , and  $\zeta_{2p\sigma}$  kept at their  $\Psi_{39}(1s, 1s', 2p\sigma)$  values] it was found that of the 25 only three configurations containing  $2p\pi$  contributed a significant lowering of the energy over  $\Psi_{17}(1s, 1s', 2p\sigma)$ . The coefficients and  $\zeta$ 's of the "best 20-configuration" wave function, denoted by  $\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$  in Table VI, are given in Table VIII, while the coefficients and  $\zeta$ 's for  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  are given in the Appendix. The electronic energies for these two wave functions are plotted in Fig. 1 (curves C and D).<sup>22</sup>

It is important to note that the ten configurations present in  $\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$  which involve two-quantum STO's are constructed of the *bonding*  $p$ -electron MO's ( $\sigma_g 2p, \pi_u 2p$ ) and the *antibonding*  $s$ -electron MO's ( $\sigma_u 1s, \sigma_u 1s'$ ). A comparison (Table VI) of the improvements in the electronic energies of  $\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$  and  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  over MO- $\zeta$  energies indicates that the improvements obtained using the former function is between 80% and 90% of that obtained with the latter.

The inclusion of superposition of configurations takes into account the energy effect of detailed correlation of the electronic positions. This correlation effect is considerably larger between two electrons in the same MO than between two electrons in different MO's. One can therefore regard the effect of superposition of configurations as modifying the single-ASOP wave function in such a way that the motions of the two electrons in the bonding MO become correlated, and similarly for the two electrons in the antibonding MO. The fact that configurations constructed of bonding two-quantum MO's are of predominant importance indicates that the correlation between the antibonding electrons is already quite well accounted for by the ten  $1s, 1s'$  configurations, while the correlation between the bonding electrons require higher-quantum correlation terms in the wave function.

Finally, the trend of the coefficients of  $\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$  (Table VIII) again emphasizes the importance of configurations involving singly-occupied MO's, and the neglect of configurations in which all the electrons are in singly-occupied MO's, results in an unfortunately high SAE. The SAE of  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  is 0.861 eV lower than the Hartree-Fock energy, 0.408 eV lower than for  $\Psi_{10}(1s, 1s')$ , but 0.97 eV higher than a pair of helium wave functions of the type  $1s1s' + \lambda 2p^2$  into which the wave function would properly go if the neglected configurations were included (Table V). Nevertheless, the separation energy of  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  includes 38% of the correlation energy.

<sup>22</sup> The  $\zeta_{2p\pi}$  which minimized the energy for  $\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$  was about 0.2 larger than the  $\zeta_{2p\pi}$  which minimized the energy for  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$ . The  $\zeta_{2p\pi}$  values reported in Table VI are those which minimize the  $\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$  energy with an error not exceeding 0.005 eV for the  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  energies (Table VII).

TABLE VIII. Coefficients, parameters and energies for  $\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$ .

Configurations	0.5 A	0.625 A	Coefficients 0.75 A	1.0 A	2.0 A
1. $(\sigma_g 1s)^2(\sigma_u 1s')^2$	+0.69763	+0.43239	+0.21942	+0.02900	-0.02917
2. $(\sigma_g 1s')^2(\sigma_u 1s)^2$	-0.01884	-0.03370	-0.05158	-0.08137	-0.02864
3. $(\sigma_g 1s)^2(\sigma_g 1s')^2$	-0.05497	-0.03352	-0.03037	-0.03477	-0.03255
4. $(\sigma_u 1s)^2(\sigma_u 1s')^2$	-0.03535	-0.03085	-0.02702	-0.02180	-0.02288
5. $(\sigma_g 1s)^2(\sigma_u 1s)^2$	-0.13694	-0.06248	-0.22167	-0.22723	-0.13463
6. $(\sigma_g 1s')^2(\sigma_u 1s')^2$	-0.04759	-0.06126	-0.08869	-0.20764	-0.10627
7. $(\sigma_g 1s)^2(\sigma_u 1s\sigma_u 1s')$	+0.33692	+0.60615	+0.70485	+0.38003	+0.17894
8. $(\sigma_u 1s)^2(\sigma_g 1s\sigma_g 1s')$	+0.07906	+0.16159	+0.25713	+0.25452	+0.16718
9. $(\sigma_g 1s')^2(\sigma_u 1s\sigma_u 1s')$	+0.04539	+0.05314	+0.08738	+0.41184	+0.50398
10. $(\sigma_u 1s')^2(\sigma_g 1s\sigma_g 1s')$	+0.01526	+0.02335	+0.08514	+0.44870	+0.48018
11. $(\sigma_g 2p)^2(\sigma_u 1s')^2$	-0.00604	-0.00606	-0.00630	-0.00729	-0.00528
12. $(\sigma_g 2p')^2(\sigma_u 1s)^2$	+0.00311	+0.00014	-0.00351	-0.00078	+0.00130
13. $(\sigma_g 2p)^2(\sigma_u 1s\sigma_u 1s')$	-0.01075	-0.01086	-0.01066	-0.01575	-0.01421
14. $(\sigma_u 1s')^2(\sigma_g 1s\sigma_g 2p)$	+0.08722	+0.07483	+0.06566	+0.03425	+0.00275
15. $(\sigma_u 1s')^2(\sigma_g 1s'\sigma_g 2p)$	+0.00828	+0.00848	+0.01048	+0.03111	+0.00426
16. $(\sigma_u 1s)^2(\sigma_g 1s\sigma_g 2p)$	-0.01298	-0.01248	-0.01289	-0.01579	-0.00115
17. $(\sigma_u 1s)^2(\sigma_g 1s'\sigma_g 2p)$	+0.00305	+0.00609	+0.00807	+0.00058	-0.00223
18. $(\pi_u 2p)^2(\sigma_u 1s')^2$	-0.02583	-0.01488	-0.00760	-0.00771	-0.00700
19. $(\pi_u 2p)^2(\sigma_u 1s)^2$	+0.00381	+0.00385	+0.00204	+0.00332	+0.00180
20. $(\pi_u 2p)^2(\sigma_u 1s\sigma_u 1s')$	-0.01471	-0.02541	-0.03024	-0.02936	-0.01851
Parameters and energies <sup>a</sup>					
$\xi_{1s}$	2.25	2.10	2.05	2.25	2.39
$\xi_{1s'}$	0.84	0.92	0.99	1.24	1.33
$\xi_{2p\sigma}$	3.4	3.2	2.8	2.5	2.5
$\xi_{2p\pi}$	3.0	2.8	2.6	2.3	2.5
$E_{e1}$ (a.u.)	-8.95744	-8.49212	-8.16625	-7.70781	-6.80024
$E_T$ (a.u.)	-4.72544	-5.10652	-5.34492	-5.59181	-5.74224

<sup>a</sup> See references 20 and 21.

With reference to the united atom, while the inclusion of MO's derived from  $2s$  STO's, and in particular  $\sigma_g 2s$ , is desirable as  $R \rightarrow 0$ , it is not important at  $0.5$  A and larger distances. However, since  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  does include configurations involving  $1s$  and  $1s'$  a proper approach to the united atom  $^1S$  of Be is guaranteed (see footnote 19).

On the basis of these considerations, then, it is estimated that the  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  electronic energy includes about 50% of the correlation energy over the region  $0.5 \text{ A} \leq R \leq 1.0 \text{ A}$ , so that the reported energy values are no more than  $1.25 \text{ ev}$  ( $0.046 \text{ a.u.}$ ) higher than the electronic energy of a completely accurate  $\text{He}_2$  wave function in this range. Since the correlation energy is roughly constant over the entire range of  $R$  (being

$2.56 \text{ ev}$  at  $R=0$  and  $2.29 \text{ ev}$  at  $R=\infty$ , see Table V), the correlation effects nearly cancel in  $V(R)=E_T(R)-2E(\text{He})$ . Thus, the values of the repulsion energy  $V_{\text{Th}}(R)$  stated and graphed in Fig. 3 is estimated to be in error by no more than  $0.6 \text{ ev}$  ( $0.022 \text{ a.u.}$ ). A least-squares fit of the  $V_{\text{Th}}(R)$  curve given in Fig. 3 yields the following representation for  $V_{\text{Th}}(R)$

$$V_{\text{Th}}(R) = 191.47e^{-3.8486R} \text{ ev} \quad 0.5 \text{ A} \leq R \leq 1.0 \text{ A}. \quad (18)$$

This expression reproduces the actual values of  $V_{\text{Th}}(R)$  at the distances  $0.5, 0.625, 0.75$ , and  $1.0 \text{ A}$  within  $0.2 \text{ ev}$ , and is to be compared with the  $a$  and  $b$  values of other authors in Table I.

#### IV. CONCLUSIONS

The  $\text{He}_2$  repulsion potential computed from  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  is plotted in Fig. 3 along with the potential reported by Amdur<sup>11</sup> for comparison. Figure 4 serves to indicate how the results deduced from experiment and the results obtained here compare with those of previous authors. It is quite evident that the large discrepancy between theory and the results deduced from scattering still essentially exists. While the initial motivation of this work was to see whether a more accurate theoretical calculation might bring agreement with experiment, it appears now that previous single-ASOP computations, especially those of Huzinaga<sup>5a</sup> and Ransil<sup>8</sup> are not nearly in as much error as the scattering results would suggest.

What has been learned is, first of all, that the descrip-

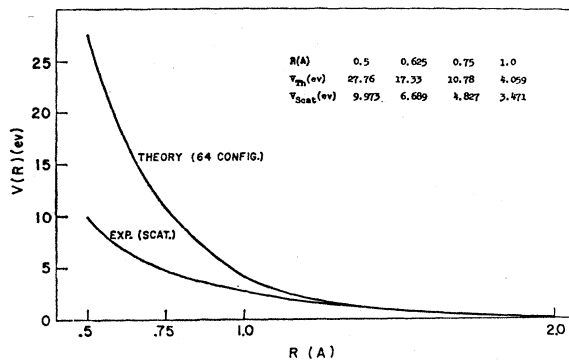


FIG. 3. Comparison of  $V(R)$  as computed from  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  and that deduced from scattering experiments (reference 11).

tion of  $\text{He}_2$  in the single-ASOP  $(1\sigma_g)^2(1\sigma_u)^2$  approximation is rather accurate, even for internuclear distances as small as 0.5 Å. Wu<sup>23</sup> has voiced the objection that since this wave function does not properly approach that of the Be united atom  $^1S$  ground state, as would be the case for  $(1\sigma_g)^2(2\sigma_g)^2$ , the computed repulsion energy in the region  $0.5 \text{ Å} < R < 1.0 \text{ Å}$  should be abnormally high. However, the fact that configurations essentially of this latter type such as  $(\sigma_g 1s)^2(\sigma_g 1s')^2$  were found to be relatively unimportant seems to remove this objection, and emphasizes the fact that even at  $R=0.5 \text{ Å}$ , the  $^1\Sigma_g^+$  ground state of  $\text{He}_2$  is still far from the united atom, and is essentially molecular in character.

The superposition of configurations treatment quantitatively has yielded repulsion energies in the region  $0.5 \text{ Å} \leq R \leq 1.0 \text{ Å}$  which differ but little from the MO- $\zeta$  results, but differ grossly from the results deduced from scattering. As pointed out by Ransil,<sup>8</sup> the present author had estimated at an early date that the discrepancy between the single configuration repulsion energies at small distances and that deduced from the scattering data were in error by about the same amount in opposite directions. It was expected at the time that a more accurate calculation would lower the repulsion energy at 0.5 Å by 5–8 ev, and that the scattering results were likewise low by 5–8 ev. However, this judgement must now be amended since the results reported here indicate the difference between the MO- $\zeta$  and the  $\Psi_{64}(1s 1s' 2p\sigma 2p\pi)$  repulsion energies at 0.5 Å is less

than 1 ev. This suggests that the scattering results are too low by about 18 ev at 0.5 Å.

On the qualitative side the preceding discussions concerning the energetic effects of added configurations should serve to indicate the directions which might be taken to further refine the present calculations. Using  $\Psi_{20}(1s 1s' 2p\sigma 2p\pi)$  as a point of departure, the inclusion of configurations of the form  $(\phi_i \phi_j \phi_k \phi_l)$  could clearly be desirable in order to obtain a good SAE. Furthermore, the inclusion of configurations containing higher-quantum bonding MO's such as  $\sigma_g 3d$  and  $\delta_g 3d$  would improve the correlation of the bonding electrons, the inclusion of  $\sigma_u 3d$  and  $\delta_u 3d$  being of lesser importance. If computations are to proceed for  $R$  values less than 0.5 Å, the inclusion of configurations containing  $\sigma_g 2s$  are clearly desirable to guarantee approach to an improved atom wave function.

On the other hand, a precise knowledge of the Hartree-Fock  $\text{He}_2$  repulsion potential would be especially useful so that the amount of correlation energy which has really been accounted for here would be accurately known. What is more important, since the correlation energy in the  $^1S$  Be ground state and in a pair of  $^1S$  helium atoms is roughly the same (Table V), it is reasonable to suppose that the correlation energy as a function of  $R$  is nearly constant for  $R \geq 0.5 \text{ Å}$ . And since the united atom configuration  $(\sigma_g 1s)^2(\sigma_g 2s)^2$  is unimportant over this same region, it seems likely that  $V(R)$  could be obtained almost exactly from the Hartree-Fock energy as a function of  $R$ , so that a more elaborate treatment which takes into account the correlation effects would serve only to improve the absolute or total energy and not the relative or repulsive energy.<sup>24</sup>

Finally, it is to be hoped that the discrepancy between these results and those of scattering will provide impetus for a reconsideration of He–He scattering processes in particular and of inert-atom repulsive interactions in general.

#### ACKNOWLEDGMENTS

The author gratefully acknowledges the active interest and immeasurable support of Professor R. S. Mulliken, who sponsored this research. He also wishes to thank Professor C. C. J. Roothaan of this laboratory and Dr. A. W. Weiss, formerly of this laboratory, for many helpful discussions.

Portions of the computations were done using machine programs constructed here by Dr. Weiss and Dr. A. D. McLean. All computations were done on the Remington-Rand Univac 1103 and 1103 A Scientific computers at Wright Air Development Division, Wright-Patterson Air Force Base, Ohio, and the cooperation of the Computation Section is gratefully acknowledged.

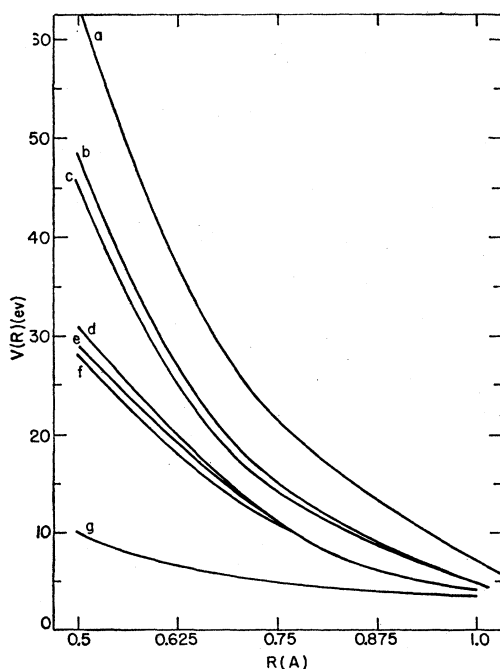


FIG. 4. Repulsion energy curves: (A) Rosen (reference 2), (B) Slater (reference 1), (C) G-W (Table II), (D) Ransil (reference 8), (E) MO- $\zeta$  (Table II), (F)  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$  (Appendix), (G) From scattering [Eq. (3)].

<sup>23</sup> Ta-Yu Wu, J. Chem. Phys. 28, 986 (1958).

<sup>24</sup> B. J. Ransil of this laboratory is extending his LCAO-SCF procedure to embrace a larger STO basis set and complete  $\zeta$ -variation flexibility so that the Hartree-Fock  $\text{He}_2$  repulsion energy should be rather accurately known in the near future (private communication).

## APPENDIX

TABLE AI. Coefficients, parameters, and energies for  $\Psi_{64}(1s, 1s', 2p\sigma, 2p\pi)$ .

Configurations <sup>a</sup>	0.5 A	0.625 A	Coefficients 0.75 A	1.0 A	2.0 A
1. $(\sigma_u 1s)^2(\sigma_u 1s')^2$	+0.66312	+0.40296	+0.19376	+0.01387	-0.02833
2. $(\sigma_g 1s')^2(\sigma_u 1s)^2$	-0.01889	-0.03488	-0.05170	-0.07258	-0.02721
3. $(\sigma_g 1s)^2(\sigma_g 1s')^2$	-0.05470	-0.03245	-0.02918	-0.03279	-0.03202
4. $(\sigma_u 1s)^2(\sigma_u 1s')^2$	-0.03799	-0.03035	-0.02464	-0.02027	-0.02271
5. $(\sigma_g 1s')^2(\sigma_u 1s)^2$	-0.12432	-0.05953	-0.21109	-0.22029	-0.13413
6. $(\sigma_g 1s')^2(\sigma_u 1s')^2$	-0.04496	-0.05648	-0.08258	-0.21473	-0.10485
7. $(\sigma_g 1s')^2(\sigma_u 1s\sigma_u 1s')$	+0.33769	+0.60404	+0.69477	+0.37790	+0.17824
8. $(\sigma_u 1s)^2(\sigma_g 1s\sigma_g 1s')$	+0.07591	+0.16145	+0.25869	+0.25180	+0.16766
9. $(\sigma_g 1s')^2(\sigma_u 1s\sigma_u 1s')$	+0.04187	+0.04893	+0.07916	+0.39776	+0.50043
10. $(\sigma_u 1s')^2(\sigma_u 1s\sigma_g 1s')$	+0.01138	+0.02028	+0.08307	+0.45501	+0.47896
11. $(\sigma_g 2p)^2(\sigma_u 1s')^2$	-0.00808	-0.00857	-0.01015	-0.01307	-0.00482
12. $(\sigma_g 2p)^2(\sigma_u 1s)^2$	+0.00514	+0.00146	-0.00201	+0.00194	+0.00221
13. $(\sigma_g 2p)^2(\sigma_u 1s\sigma_u 1s')$	-0.01412	-0.01305	-0.01226	-0.01492	+0.01361
14. $(\sigma_u 1s')^2(\sigma_g 1s\sigma_g 2p)$	+0.08480	+0.07100	+0.05975	+0.03212	+0.00297
15. $(\sigma_u 1s')^2(\sigma_g 1s'\sigma_g 2p)$	+0.00758	+0.00746	+0.00849	+0.02787	+0.00426
16. $(\sigma_u 1s)^2(\sigma_g 1s\sigma_g 2p)$	-0.01545	-0.01389	-0.01268	-0.01576	-0.00133
17. $(\sigma_u 1s)^2(\sigma_g 1s'\sigma_g 2p)$	+0.00216	+0.00591	+0.00915	-0.00398	-0.00221
18. $(\sigma_g 2p)^2(\sigma_g 1s)^2$	-0.00999	-0.01309	-0.01364	+0.00017	+0.00260
19. $(\sigma_g 2p)^2(\sigma_g 1s')^2$	+0.00185	+0.00233	+0.00326	-0.00039	-0.00440
20. $(\sigma_g 2p)^2(\sigma_g 1s\sigma_g 1s')$	-0.00480	-0.00746	-0.01290	-0.01269	-0.01269
21. $(\sigma_g 1s)^2(\sigma_g 1s'\sigma_g 2p)$	-0.00064	-0.00622	-0.01185	-0.00934	-0.00046
22. $(\sigma_g 1s')^2(\sigma_g 1s\sigma_g 2p)$	-0.00850	-0.00539	-0.00439	+0.00064	+0.00015
23. $(\sigma_u 2p)^2(\sigma_g 1s)^2$	-0.02257	-0.01927	-0.01991	-0.00350	+0.00211
24. $(\sigma_u 2p)^2(\sigma_g 1s')^2$	-0.00391	-0.00215	-0.00151	-0.00356	-0.00471
25. $(\sigma_u 2p)^2(\sigma_g 1s\sigma_g 1s')$	+0.01083	+0.00575	+0.00109	-0.01310	-0.01264
26. $(\sigma_g 1s)^2(\sigma_u 1s\sigma_u 2p)$	+0.01510	+0.00133	-0.00787	-0.00014	+0.00965
27. $(\sigma_g 1s)^2(\sigma_u 1s'\sigma_u 2p)$	-0.05464	-0.04060	-0.03531	-0.01718	+0.00771
28. $(\sigma_g 1s')^2(\sigma_u 1s\sigma_u 2p)$	-0.00416	-0.00578	-0.00704	-0.00718	-0.00197
29. $(\sigma_g 1s')^2(\sigma_u 1s'\sigma_u 2p)$	+0.00030	+0.00396	+0.00392	-0.01249	-0.00317
30. $(\sigma_u 2p)^2(\sigma_u 1s)^2$	+0.00090	+0.00119	+0.00152	+0.00294	+0.00223
31. $(\sigma_u 2p)^2(\sigma_u 1s')^2$	-0.00460	-0.00184	-0.00067	-0.00127	-0.00372
32. $(\sigma_u 2p)^2(\sigma_u 1s\sigma_u 1s')$	-0.00265	-0.00441	-0.00658	-0.00980	-0.01134
33. $(\sigma_u 1s)^2(\sigma_u 1s'\sigma_u 2p)$	+0.00265	+0.00317	+0.00339	+0.00111	-0.00029
34. $(\sigma_u 1s')^2(\sigma_u 1s\sigma_u 2p)$	-0.00869	-0.00406	-0.00189	+0.00052	+0.00004
35. $(\sigma_g 2p)^2(\sigma_u 2p)^2$	-0.00239	-0.00296	-0.00357	-0.00211	-0.00049
36. $(\sigma_g 2p)^2(\sigma_u 1s\sigma_u 2p)$	+0.00122	-0.00005	-0.00142	-0.00171	-0.00030
37. $(\sigma_g 2p)^2(\sigma_u 1s'\sigma_u 2p)$	-0.00730	-0.00684	-0.00729	-0.00577	-0.00051
38. $(\sigma_u 2p)^2(\sigma_g 1s\sigma_g 2p)$	+0.00750	+0.00978	+0.01162	+0.00612	+0.00036
39. $(\sigma_u 2p)^2(\sigma_g 1s'\sigma_g 2p)$	+0.00162	+0.00176	+0.00256	+0.00507	+0.00060
40. $(\pi_u 2p)^2(\sigma_u 1s)^2$	+0.00414	+0.00464	+0.00304	+0.00430	+0.00300
41. $(\pi_u 2p)^2(\sigma_u 1s')^2$	-0.02420	-0.01357	-0.00657	-0.00669	-0.00613
42. $(\pi_u 2p)^2(\sigma_u 1s\sigma_u 1s')$	-0.01455	-0.02508	-0.02398	-0.02832	-0.01771
43. $(\pi_u 2p)^2(\sigma_g 1s)^2$	-0.00773	-0.01005	-0.00836	+0.00309	+0.00329
44. $(\pi_u 2p)^2(\sigma_g 1s')^2$	+0.00479	+0.00417	+0.00455	+0.00040	-0.00624
45. $(\pi_u 2p)^2(\sigma_g 1s\sigma_g 1s')$	-0.00788	-0.01028	-0.01549	-0.02518	-0.01758
46. $(\pi_g 2p)^2(\sigma_u 1s)^2$	+0.00196	+0.00282	+0.00293	+0.00449	+0.00324
47. $(\pi_g 2p)^2(\sigma_u 1s')^2$	+0.00606	-0.00350	-0.01435	-0.00255	-0.00554
48. $(\pi_g 2p)^2(\sigma_u 1s\sigma_u 1s')$	-0.00551	-0.01046	-0.01396	-0.01678	-0.01669
49. $(\pi_g 2p)^2(\sigma_g 1s)^2$	-0.01003	-0.01344	-0.01345	-0.00190	+0.00290
50. $(\pi_g 2p)^2(\sigma_g 1s')^2$	+0.00155	+0.00193	+0.00255	-0.00114	-0.00671
51. $(\pi_g 2p)^2(\sigma_g 1s\sigma_g 1s')$	-0.00371	-0.00626	-0.01101	-0.02288	-0.01808
52. $(\pi_g 2p)^2(\sigma_g 1s'\sigma_g 2p)$	+0.00034	+0.00055	+0.00079	+0.00100	+0.00069
53. $(\pi_g 2p)^2(\sigma_g 1s\sigma_g 2p)$	-0.00084	-0.00122	-0.00158	-0.00114	-0.00012
54. $(\pi_g 2p)^2(\sigma_g 1s'\sigma_g 2p)$	-0.00028	-0.00030	-0.00032	-0.00086	-0.00013
55. $(\pi_u 2p)^2(\sigma_u 2p)^2$	+0.00061	+0.00058	+0.00075	+0.00080	+0.00064
56. $(\pi_u 2p)^2(\sigma_u 1s\sigma_u 2p)$	-0.00013	+0.00048	+0.00087	+0.00036	0.00000
57. $(\pi_u 2p)^2(\sigma_u 1s'\sigma_u 2p)$	+0.00197	+0.00125	+0.00104	+0.00103	+0.00001
58. $(\pi_g 2p)^2(\sigma_u 2p)^2$	+0.00033	+0.00037	+0.00052	+0.00061	+0.00063
59. $(\pi_g 2p)^2(\sigma_u 1s\sigma_u 2p)$	+0.00018	+0.00038	+0.00054	+0.00017	-0.00001
60. $(\pi_g 2p)^2(\sigma_u 1s'\sigma_u 2p)$	+0.00050	+0.00030	+0.00030	+0.00051	0.00000
61. $(\pi_u 2p)^2(\sigma_g 2p)^2$	+0.00070	+0.00099	+0.00129	+0.00132	+0.00070
62. $(\pi_u 2p)^2(\sigma_g 1s\sigma_g 2p)$	-0.00140	-0.00209	-0.00272	-0.00180	-0.00013
63. $(\pi_u 2p)^2(\sigma_g 1s'\sigma_g 2p)$	-0.00057	-0.00036	-0.00006	-0.00083	-0.00014
64. $(\pi_g 2p)^2(\pi_u 2p)^2$	+0.00020	+0.00092	+0.00115	+0.00135	+0.00102
Parameters and energies					
$\xi_{1s}$	2.25	2.10	2.05	2.25	2.39
$\xi_{1s'}$	0.84	0.92	0.99	1.24	1.33
$\xi_{2p\sigma}$	3.4	3.2	2.8	2.5	2.5
$\xi_{2p\pi}$	3.0	2.8	2.6	2.3	2.5
$E_{e1}$ (a.u.)	-8.96695	-8.50386	-8.18023	-7.72183	-6.81759
$E_T$ (a.u.)	-4.73495	-5.11826	-5.35890	-5.60583	-5.75379
$V(R)$ (ev) <sup>b</sup>	27.76	17.33	10.78	4.059	0.0329

<sup>a</sup>  $\Psi_{10}(1s, 1s')$ , composed of configurations 1-10;  $\Psi_{17}(1s, 1s', 2p\sigma)$ , of configurations 1-17;  $\Psi_{19}(1s, 1s', 2p\sigma)$ , of configurations 1-39;  $\Psi_{20}(1s, 1s', 2p\sigma, 2p\pi)$ , of configurations 1-17, 40-42.

<sup>b</sup> Separation energy -5.755 a.u. (Table IV.)