## Lowest ${}^{3}\Delta_{u}$ state of He<sub>2</sub>

N. C. Bacalis

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vassileos Constantinou 48, GR - 11635 Athens, Greece

(Received 24 August 1992)

The He<sub>2</sub> molecule is examined in the  ${}^{3}\Delta_{u}$  symmetry via the numerical Hartree-Fock method. A previously unreported state is found with lower energy than states reported in the literature, necessitating a reassessment of the question of the stability of corresponding "daughter" states of the He<sub>2</sub><sup>-</sup> ion.

PACS number(s): 31.20.Di, 31.20.Ej, 31.50.+w

The He<sub>2</sub><sup>-</sup> ion has been reported to be relatively stable in two metastable states,  ${}^{4}\Pi_{g}$  [1] and  ${}^{4}I_{g}$  [2]. Both are characterized by the same He<sub>2</sub><sup>+</sup> core  $(1\sigma_{g}^{2}1\sigma_{u})$  to which the two outer electrons are attached in diffuse bonding orbitals of consecutive angular-momentum quantum numbers. The relative stability of these states is determined with respect to their "parent" states of the neutral He<sub>2</sub> molecule.

In examining the relative stability of the metastable states  ${}^{4}\Phi_{g}$  and  ${}^{4}I_{g}$  of the He<sub>2</sub><sup>-</sup> ion Adamowicz and Pluta [2] have calculated self-consistently the correspond-ing parent states of He<sub>2</sub>  ${}^{3}\Pi_{g}$ ,  ${}^{3}\Delta_{u}$ , and  ${}^{3}\Phi_{g}$ , by the computer program PWMCSCF of McCullough and Adamowicz [3], in the single-configuration restricted Hartree-Fock approximation, where the corresponding configu-rations are He<sub>2</sub><sup>-</sup>  ${}^{4}\Phi_{g}$ :  $(1\sigma_{g}^{2}1\sigma_{u}1\pi_{u}1\delta_{g})$ , He<sub>2</sub><sup>-</sup>  ${}^{4}I_{g}$ :  $(1\sigma_q^2 1\sigma_u 1\delta_g 1\phi_u)$ ; and the parent states: He<sub>2</sub>  $^{3}\Pi_{g}$ :  $(1\sigma_g^2 1\sigma_u 1\pi_u)$ , He<sub>2</sub>  $^{3}\Delta_u$ :  $(1\sigma_g^2 1\sigma_u 1\delta_g)$ , and He<sub>2</sub>  $^{3}\Phi_g$ :  $(1\sigma_{q}^{2}1\sigma_{u}1\phi_{u})$ . In all of these states the first two orbitals are very similar to the ones of the He<sub>2</sub> +  ${}^{2}\Sigma_{u}^{+}$ :  $(1\sigma_a^2 1\sigma_u)$  state, while the outer orbitals are quite diffuse in both the parent neutral and the ionic states. Typical values reported [2] for the total energy of the neutral He<sub>2</sub> molecule, its orbital energies, and the squared distance  $\langle R^2 \rangle$  of the outer electron from the center of the molecule are shown in Table I for the equilibrium internuclear separation  $(R_{ab} = 2 \text{ a.u.})$ . The self-consistent-field (SCF) calculation converges to these values starting from reasonable initial guesses. However, the results emerging from the  $1\delta_q$  orbital exhibit the unexpected feature that they do not lie between those arising from the  $1\pi_u$  and the  $1\phi_u$  orbitals (Table I).

Since the calculation is numerical, i.e., it makes use of molecular diatomic orbitals expanded in partial waves expressed in spheroidal prolate coordinates [3] [thus avoiding expansion of the orbitals in (unknown) basis sets] it is often advantageous [4] to treat the initial guess directly as numerical one-electron diatomic molecular orbitals (OEDMO) rather than as a linear combination of atomic orbitals [3], because then the character of each orbital can be directly controlled. In the present work the use of OEDMO's as an initial guess to the SCF calculation [3] has been adopted either for all orbitals or, at



FIG. 1. The self-consistent (SCF) orbitals involved in the He<sub>2</sub>  $^{3}\Delta_{u}$  states of the present work (without nodes) and of Ref. [2] (with one node), represented by the points, compared with corresponding one-electron diatomic molecular orbitals (OEDMO), represented by the lines. The  $\xi$  variable is  $\xi = (r_a + r_b)/R_{ab}$ , where  $r_a$  and  $r_b$  are the distances of the electron from the two nuclei a and b, and  $R_{ab}$ is the internuclear distance  $(R_{ab} = 2 \text{ a.u.})$ .  $X_1(\xi)$  (represented by points) is the first (and main) term in a partial-wave expansion [3] of the SCF orbital wave function  $\Psi_{\rm SCF}(\xi,\eta,\phi) = \Sigma_{lm} X_l(\xi) Y_{lm}(\eta,\phi)$ , where  $\eta = (r_a - r_b)/R_{ab}$ ,  $\phi$  is the azimuthal angle of the electron position, and  $Y_{lm}$  are spherical harmonics. The solid and dashed curves represent, respectively, the OEDMO's  $1\delta_g$  and  $2\delta_g$  [defined by (nlm)] united-atom quantum numbers (322) and (422), respectively] computed [4] with effective nuclear charges  $z_a^* = z_b^* = 0.5$ a.u.  $\Xi(\xi)$  (represented by lines) is the radial-like part of the OEDMO wave function  $\Psi_{OEDMO}(\xi, \eta, \phi) = \Xi(\xi)H(\eta)e^{im\phi}$ . The figure suggests that the SCF  $\delta_g$  of the present work is practically  $1\delta_g$ , whereas that of Ref. [2] is the  $2\delta_g$ .

1050-2947/93/47(6)/5206(3)/\$06.00

<u>47</u> 5206

TABLE I. Three neutral He<sub>2</sub> states as reported in Ref. [2]. Typical values of the total Hartree-Fock (HF) energy, the orbital energies, and the squared distance of the outer electron from the center of the molecule, at the equilibrium interatomic separation of 2 a.u. For the  ${}^{3}\Delta_{u}$  state the corresponding values from the present work are also displayed. (All quantities in a.u.)

					The second s	
State	Outer orbital	$E_{ m HF}$	$\varepsilon(1\sigma_g)$	$\varepsilon(1\sigma_u)$	$\varepsilon_{\mathrm{outer}}$	$\langle R^2 \rangle_{ m outer}$
$^{3}\Pi_{g}$	$1\pi_u$	-5.051	-1.42	-1.21	-0.13	27.5
$^{3}\Delta_{u}$	$1\delta_g$	-4.954	-1.61	-1.40	-0.03	515.3
	$1\delta_g^{\mathbf{a}}$	-4.978	-1.57	-1.35	-0.05	130.2
${}^{3}\Phi_{g}$	$1 \check{\phi_u}$	-4.954	-1.61	-1.40	-0.03	364.4

<sup>a</sup>This work.

least, for the most diffuse ones.

In this paper it is shown that whereas some starting choices of the  $\delta_g$  orbital lead to the results of Ref. [2], some other special choices may lead to lower energy. By using as an initial choice the  $1\delta_g$  OEDMO, defined by the united-atom quantum numbers (UAQN) (nlm) =(322), with the appropriate nuclear charge screening, it is possible to achieve convergence for the state He<sub>2</sub>  $^{3}\Delta_{u}$ to energy values (Table II) which are lower than those reported in Ref. [2] by about 0.02 a.u. at all internuclear separations, and which indeed lie between those of He<sub>2</sub>  ${}^{3}\Pi_{g}$  and He<sub>2</sub>  ${}^{3}\Phi_{g}$ . On the other hand, the choice of the  $2\delta_q$  OEDMO [with UAQN (nlm) = (422)] as an initial guess with a variety of nuclear charge screenings, leads to the [higher] SCF values reported in Ref. [2], or even higher. It should be noted that the choice of the  $1\delta_q$  OEDMO as an initial guess does not by itself guarantee convergence to the lower-lying state; it is essential to use appropriate nuclear charge screening, otherwise  $1\delta_g$ leads again to higher SCF values, either those of Ref. [2] or even higher. The difficulty encountered at determining the SCF lower energy of the He<sub>2</sub>  $^{3}\Delta_{u}$  state within the Hartree-Fock iterative scheme suggests that this state is, in the language of nonlinear phenomena, an attractor whose basin of attraction has a more limited extent than the higher-energy state of Ref. [2], and that other higherlying states are accessible from a much wider variety of initial conditions.

The character of the SCF  $\delta_g$  orbitals involved in the lower He<sub>2</sub>  ${}^{3}\Delta_u$  state, reported here, and the higher one of Ref. [2], is shown in Fig. 1, for  $R_{ab} = 2$  a.u. The orbital of Ref. [2] has one node and thus corresponds to the  $2\delta_g$  whereas the present one has no nodes and corresponds to the  $1\delta_g$ . For comparison, the pure OEDMO's  $1\delta_g$  and  $2\delta_g$  [defined by (nlm) UAQNs (322) and (422), respective] computed [4] with effective nuclear charges  $z_a^* = z_b^* = 0.5$  a.u. are also displayed. They are practically identical with the corresponding SCF orbitals of the two He<sub>2</sub>  ${}^{3}\Delta_u$  states in question. Furthermore, the squared distance  $\langle R^2 \rangle$  for these two OEDMO's equals 130.4 and 515.7 a.u., respectively, in remarkable agreement with the SCF values at  $R_{ab} = 2$  a.u.. Hence one can conclude that the Hartree-Fock configuration of the lower He<sub>2</sub>  ${}^{3}\Delta_u$  state is  $(1\sigma_g^2 1\sigma_u 1\delta_g)$  whereas that of the higher one (reported in Ref. [2]) is  $(1\sigma_a^2 1\sigma_u 2\delta_g)$ .

A similar treatment of the He<sub>2</sub>  ${}^{3}\Pi_{g}$  and He<sub>2</sub>  ${}^{3}\Phi_{g}$ states as well as the He<sub>2</sub>  ${}^{-4}\Phi_{g}$  and He<sub>2</sub>  ${}^{-4}I_{g}$  states did not reveal any other attractor than those reported in Ref. [2].

As a corollary there should be a reassessment of the question of the boundedness of the He<sub>2</sub><sup>-4</sup> $I_g$  metastable

TABLE II. Total Hartree-Fock (HF) energies, occupied orbital energies, and expectation values of  $\langle R^2 \rangle$  of the  $1\delta_g$  orbital (all in a.u.) for the He<sub>2</sub>  ${}^3\Delta_u$ :  $(1\sigma_g^2 1\sigma_u 1\delta_g)$  state as a function of the internuclear separation  $R_{ab}$ .

<b>D</b> .		a(1-)	-(1 - )	-(15)	(D <sup>2</sup> )(16)
nab	L'HF	$\varepsilon(1\sigma_g)$	$\varepsilon(1\sigma_u)$	$\varepsilon(10_g)$	$\langle R^{-}\rangle(10_{g})$
0.5	-2.575887	-3.39631	-0.50136	-0.057073	117.6
0.7	-3.841682	-2.85017	-0.62026	-0.056406	121.2
1.0	-4.562558	-2.29011	-0.86277	-0.055788	124.6
1.4	-4.888717	-1.87757	-1.13702	-0.055229	127.2
1.6	-4.946615	-1.74735	-1.23034	-0.055140	128.2
1.8	-4.971656	-1.64667	-1.29918	-0.054961	129.2
2.0	-4.977913	-1.56714	-1.34896	-0.054787	130.2
2.2	-4.973931	-1.50328	-1.38437	-0.054614	131.2
2.4	-4.964874	-1.45133	-1.40907	-0.054444	132.2
2.6	-4.953807	-1.40862	-1.42583	-0.054274	133.1
3.0	-4.931858	-1.34354	-1.44337	-0.053933	135.1
4.0	-4.896782	-1.25064	-1.44440	-0.053034	140.5
5.0	-4.883651	-1.20575	-1.43069	-0.052025	146.9
6.0	-4.878938	-1.18107	-1.41887	-0.050921	154.2
7.0	-4.876754	-1.16587	-1.41069	-0.049765	162.4

TABLE III. Total Hartree-Fock (HF) energies (in a.u.) of the He2  ${}^{3}\Pi_{g}$ ,  ${}^{3}\Delta_{u}$ , and  ${}^{3}\Phi_{g}$  and theHe2  ${}^{-4}\Phi_{g}$  and  ${}^{4}I_{g}$  states at  $R_{ab} = 2$  a.u.He2 stateEHFHe2  ${}^{-5}$  stateEHF

He <sub>2</sub> state	$E_{ m HF}$	He <sub>2</sub> <sup>-</sup> state	$E_{ m HF}$
$^{3}\Pi_{g}$ : $(1\sigma_{g}^{2}1\sigma_{u}1\pi_{u})$	-5.0512		
		${}^{4}\Phi_{g}$ : $(1\sigma_{g}^{2}1\sigma_{u}1\pi_{u}1\delta_{g})$	-4.9818
$^{3}\Delta_{u}$ : $(1\sigma_{g}^{2}1\sigma_{u}1\delta_{g})$	-4.9779		
3 - (2 )		${}^{*}I_{g}$ : $(1\sigma_{g}^{z}1\sigma_{u}1\delta_{g}1\phi_{u})$	-4.9544
$^{\circ}\Phi_g: (1\sigma_g^* 1\sigma_u 1\phi_u)$	-4.9542		

state [2]. The results presented in Table III (for  $R_{ab} = 2$  a.u.) suggest that both ionic He<sub>2</sub><sup>-</sup>  ${}^{4}\Phi_{g}$  and He<sub>2</sub><sup>-</sup>  ${}^{4}I_{g}$  metastable states are unbound with respect to one of their neutral parent states.

Professor E.A. McCullough, who has kindly provided our institute with the program PWMCSCF, is gratefully acknowledged.

- Y.K. Bae, M.J. Coggiola, and J.R. Peterson, Phys. Rev. Lett. 52, 747 (1984); T.J. Klave, R.N. Compton, G.D. Alton, J.S. Thompson, and D.J. Pegg, Phys. Rev. Lett. 56, 582 (1986).
- [2] L. Adamowicz and T. Pluta, Chem. Phys. Lett. 179, 517 (1991).
- [3] L. Adamowicz and E.A. McCullough, Jr., J. Chem. Phys. 75, 2475 (1981); E.A. McCullough, Jr., Comput. Phys. Rep. 4, 267 (1986); Chem. Phys. Lett. 24, 55 (1974); J. Chem. Phys. 62, 3991 (1975).
- [4] N.C. Bacalis, Y. Komninos and Cl. A. Nicolaides, Phys. Rev. A 45, 2701 (1992).