Combined CI-HY Studies of Atomic States. IV. The Four Lowest ^1S and Four Lowest ^1P States of He and the Lowest ^1S and ^1P States of H⁻

JAMES S. SIMS, STANLEY A. HAGSTROM, AND JOHN R. RUMBLE, JR.*

Chemistry Department, Indiana University, Bloomington, Indiana 47401, USA

Abstracts

Combined CI-HY method calculations are reported for the ground and first three excited S states of He with an error on the order of 10^{-7} a.u. within the same 120-term basis. For He ^1P, the four lowest states are obtained with an error $\leq 2 \times 10^{-6}$ a.u. within the same 102-term basis. H⁻ ^1S and ^1P states are also treated by the same CI-HY technique. The utility of an *spd* Slater-type orbital, r_{ij}^v, $v = 0, 1$ basis is investigated, with indications that it might be an excellent basis for states of first row atoms.

On présente des calculs CI-HY (interaction de configurations combinée avec la méthode de Hylleraas) pour l'état fondamental et les trois premiers états S excités de He avec une erreur de l'ordre de grandeur 10^{-7} u.a. dans le cadre de la même base (120 termes). Pour He, ^1P les quatre états les plus bas sont obtenus avec une erreur $\leq 2 \times 10^{-6}$ u.a. par une base de 102 termes. Les états ^1S et ^1P de H⁻ sont traités par la même méthode. On a étudié l'utilisation d'une base avec des orbitales de type de Slater *spd* et r_{ij}^v, $v = 0, 1$, ce qui indique que cela pourrait fournir une base excellente pour les états des atomes de la première ligne.

Es werden CI-HY-Berechnungen (Konfigurationswechselwirkung kombiniert mit der Hylleraas'schen Methode) für den Grundzustand und die drei ersten angeregten S-Zustände des He-Atoms vorgelegt. Mit den angewandten Basissatz (120 Glieder) ist der Fehler von der Grössenordnung 10^{-7} at.E. Für He, ^1P werden die vier tiefsten Zustände mit einem Fehler $\leq 2 \times 10^{-6}$ at.E. im einem 102-gliedrigen Basissatz erhalten. S-und P-Zustände für H⁻ werden derselben Methode behandelt. Die Anwendbarkeit eines Basissatzes mit Slaterorbitalen von *spd*-Type und r_{ij}^v, $v = 0, 1$ wird untersucht; dieses möchte eine vortreffliche Basis für die Zustände der Atome der ersten Zeile bilden.

1. Introduction

There are two standard variational methods for accounting for correlation effects in atomic states. The configuration-interaction (CI) method is based on products of one-electron functions, while the Hylleraas (HY) method explicitly includes the interelectronic coordinates r_{ij} in the terms of the wave function. The latter method has been used to obtain extremely accurate wave functions for two-electron atomic states. For three-electron atomic states, Larsson [1] performed a very accurate calculation on the ground state and showed the usefulness of the HY method expansions for the excited S states as well [2]. Perkins has carried out low-order HY method calculations on some He [3] and Li [4] excited S states as well as on the ground state of beryllium [5]. We have shown that HY

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expansions may readily be combined with conventional CI methods to yield results of relatively high accuracy [6] for three-electron [7] and four-electron [6, 8] ground and excited states. These CI-HY expansions have proven useful for computing upper and lower bounds to transition probabilities [9], electric polarizabilities, along with rigorous lower bounds [10], and Stieltjes imaging of photodispersion profiles [11]. Since the most accurate helium wave functions of Kinoshita [12], Pekeris [13], Schwartz [14], Ermolaev and Sochilin [15], Frankowski and Pekeris [16], and others lead to very difficult integrals for three or more electrons, we felt it would be important to keep the CI-HY form and investigate several ground and excited ^1S and ^1P states of helium and H$^-$ with various Slater-type orbital (STO) times r_{ij}^n bases.

2. Wave-Functions

The wave-functions were obtained by a variational solution to the Schrödinger equation, $\mathscr{H}\Psi = E\Psi$, where $\mathscr{H}$ is the nonrelativistic spin-independent Hamiltonian

$$\mathscr{H} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - Z/r_1 - Z/r_2 + 1/r_{12} \tag{1}$$

in Hartree atomic units* and Z is the nuclear charge. The trial wave-functions are of the form

$$\Psi_{\text{He,H}^-}(X_1, X_2) = \sum_K C_K \Phi_K(X_1, X_2) \tag{2}$$

where $X_i = (\mathbf{r}_i, \xi_i)$ is the combined space-spin coordinate for electron i, and where

$$\Phi_K = O(L^2)O_{\text{as}}\left(\chi r_{12}^{v_K} \prod_{s=1}^{2} \varphi_{Ks}(\mathbf{r}_s)\right) \tag{3}$$

In Eq. (3), $O(L^2)$ is an idempotent orbital-angular momentum projection operator [17] and O_{as} is the projection operator which guarantees the antisymmetry of the wave-function, i.e.,

$$O_{\text{as}} = (2!)^{-1} \sum_p (-1)^p P = (2!)^{-1}(1 - P_{12}) \tag{4}$$

Also, χ is the two-electron spin function corresponding to $S = S_Z = 0$: $\chi = (1/\sqrt{2})$ $(\alpha_1\beta_2 - \beta_1\alpha_2)$. In Eq. (3), $\varphi_{Ks}(\mathbf{r}_s)$ refers to the sth basis orbital in the Kth configuration. The orbital basis consists of STO's of the general form

$$\varphi(\mathbf{r}) = \frac{(2\xi)^{n+1/2}}{[(2m)!]^{1/2}} r^{n-1} e^{-\xi r} Y_{l,m}(\theta, \varphi) \tag{5}$$

where the set $\{Y_{l,m}\}$ consists of normalized spherical harmonics in the dirac phase convention [18].

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* In Hartree atomic units, the unit of energy is chosen as $m_e e^4/\hbar^2 \equiv 1$ a.u. (of energy) $\equiv 1\ H$, with m_e being the mass of the electron.

In the two-electron cases of He and H⁻, spin can be eliminated from the problem. Defining $F_K = r_{12}^{v_K}\varphi_{K1}(\mathbf{r}_1)\varphi_{K2}(\mathbf{r}_2)$, the explicit formula for the Hamiltonian matrix element after integration over spin coordinates is [6]

$$H_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle$$

$$= (1/2!)\langle O(L^2)S_1' F_K | \mathcal{H} | S_1' F_L \rangle \qquad (6)$$

where $S_1' = (1\sqrt{2})(1 + P_{12}')$ is a normalized space pair symmetrizer. Expanding,

$$H_{KL} = (1/2!)\{2\langle O(L^2)F_K|\mathcal{H}|F_L\rangle + \langle O(L^2)P_{12}'F_K|\mathcal{H}|F_L\rangle + \langle O(L^2)F_K|\mathcal{H}|P_{12}F_L\rangle\} \qquad (7)$$

and Eq. (7) reduces to one term if F_K and F_L are symmetric with respect to interchange of electron coordinates 1 and 2.

3. Results and Discussion

In the following He and H⁻ calculations we will examine various *spdf* STO, r_{12}^v ($v = 0, 1, 2$) bases.

A. ¹P States

For ¹P states, the space part of our trial wave functions are of the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_K C_K \Phi_K(\mathbf{r}_1, \mathbf{r}_2) \qquad (8)$$

with the basis functions specifically of the form

$$\Phi_K(\mathbf{r}_1, \mathbf{r}_2) = (1 + P_{12})r_1^{n_{K1}-1}r_2^{n_{K2}-1} e^{-\xi_{K1}r_1 - \xi_{K2}r_2}r_{12}^{v_K} Y_0^0(\theta_1, \varphi_1)Y_1^0(\theta_2, \varphi_2) \qquad (9)$$

where Y_1^0 is the ($m = 0$) spherical harmonic chosen to give $P(l = 1)$ symmetry, so that no $O(L^2)$ projection is required. Thus, each configuration is a product of the *s* STO and a p_o STO. There remains the choice of sp_o STO basis functions and choice of configurations in the expansion given by Eq. (8). We will consider the He ¹P states first, then H⁻ ¹P states.

1. *He* ¹*P*. For our initial basis orbitals we chose the STO sets $1s, 2s, \ldots, 5s$; $2p, 3p, \ldots, 9p$,* which correspond to two nonlinear parameters, the orbital exponent ξ_{ns} for the *ns* set and the orbital exponent ξ_{mp} for the *mp* set. To fix these two parameters, we optimized ξ_{ns} and ξ_{mp} for an 18-term wave function consisting of all *ns mp* r_{12}^v terms corresponding to $n = 1, 2, 3$, $m = 2, 3$, $v = 0, 1, 2$.† The result was the 18-term result listed in Table I, with $\xi_{ns} = 2.12757$, $\xi_{mp} = 0.62512$. These exponents were adopted for the *ns*, *mp* sets referred to earlier. Adding a $4p$ orbital ($\xi_{4p} = 0.62512$) led to an additional nine *ns mp* r_{12}^v terms and the 27-term

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* In the notation we are using, priming on functions of the same symmetry refers to different values of ξ; e.g., $1s, 2s, 1s', 1s''$ means a set of STO's with orbital exponents of $\xi_{1s} = \xi_{2s} \neq \xi_{1s'} \neq \xi_{1s''}$.

†The optimization was carried out with STEPIT, a Quantum Chemistry Program Exchange (#66) program for optimization of a function with respect to nonlinear parameters. The program is available from QCPE, Indiana University, Bloomington, In. 47401.

TABLE I.   Energies E (a.u.) for helium ^1P wave-functions.

Number of terms	State			
	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
This work				
18	−2.12368544			
27	−2.12379121	−2.051888	−1.976336	
30	−2.12382327	−2.05427147	−2.00850123	
45	−2.12383836	−2.05510553	−2.02624795	
57	−2.12384095	−2.05514557	−2.03058046	−2.00995064
90	−2.12384194	−2.05514605	−2.03106235	−2.0186399
102	−2.12384199	−2.05514607	−2.03106736	−2.01990994
Pekeris et al. [19]				
56	−2.12384036	−2.05512626	−2.03102731	−2.01984938
120	−2.12384287	−2.05514430	−2.03106116	−2.01988658
220	−2.12384306	−2.05514612	−2.03106817	−2.01990119
Exact [19, 24]	−2.12384309	−2.05514636	−2.03106959	−2.01990572
Anderson and Weinhold [20]				
	−2.12384303	−2.05514560	−2.03106564	
Green et al. [25]				
				−2.019905

result listed in Table I. Next, a $5p$ orbital was added and a few energetically unimportant terms were dropped, resulting in a 30-term result (Table I), and then $6p$, $7p$ orbitals were added, leading to the 45-term result. At this point, in order to increase the flexibility of our basis, particularly with respect to the higher roots, we choose a p' orbital ($\xi_{p'} = 0.41675$) and added an $8p$ orbital, leading to the 57-term results listed in Table I. For comparison purposes, the results of Pekeris et al. [19] are listed for various expansion lengths. In the Pekeris calculations, separate wave functions are computed for each $N\,^1P$ wave function, whereas our results are obtained for different roots within the same basis. Note that our 57-term results at this point are better than the 56-term Pekeris et al. expansion for $2\,^1P$, and better than the Pekeris et al. 120-term expansion for the $3\,^1P$ state. Since we were interested in obtaining good roots for ground and excited states within the same basis, we shifted our attention at this point to excited states. Since the function $re^{-0.62512}\,Y_1^0$ had proven suitable for a $2p$ orbital, we chose parameters as fractions of 1.35024, i.e., we chose $\xi_{p'} = 1.35024/3 = 0.41675$, $\xi_{p''} = 1.35024/4 = 0.31255$ as exponents for $m'p'$, $m''p''$ orbitals to improve the description of (primarily) the excited ^1P states. Various $ns\,mp\,r_{12}^v$, $ns\,m'p'\,r_{12}^v$, $ns\,m''p''\,r_{12}^v$ configurations were added to the 57-term until the 90-term result listed in Table I was obtained. This wave-function, which describes not only the lowest state of ^1P symmetry, but also other excited ^1P states as well, has proven ideal for Stieltjes imaging of He

photodispersion profiles [11]. Finally, we added an $\xi_p$iv = 0.25005 exponent and orbitals and terms derived from it in order to better describe the 4 ^1P and 5 ^1P states, leading to the final 102-term results listed in Table I. Note that the final wave function gets the first three ^1P states with energies on the order of 10^{-6} a.u. or better ($\Delta E = 1 \times 10^{-6}$, 3×10^{-7}, 2×10^{-6}, respectively) with the 2 ^1P wave-function quality (energetically) on a level approaching the 120-term Pekeris et al. [11] expansion, and the 3 ^1P and 4 ^1P results approaching the level of the Pekeris et al. [19] 220-term expansions. For comparison purposes, we also list the 137-term results of Anderson and Weinhold [20] (AW), who employ expansions similar to ours but with fewer nonlinear parameters and who do each state separately, as do Pekeris et al. [19]. From Table I, we see that our 102-term wave function gives wave functions energetically superior to the Weinhold 3 ^1P and 4 ^1P 135-term expansions. In Table I, the italic portions of the eigenvalues in AW and our final results are those digits which differ from the accurate eigenvalues as calculated by Pekeris et al. [19]. The eigenvalues calculated here are seen to be of high quality, especially for the lower 3–4 states of ^1P symmetry, and are consider-ably more compact than corresponding Pekeris et al. wave functions of equivalent accuracy. Additionally, the fact that we have obtained four roots of high quality may have advantages in computing upper and lower bounds to oscillator strengths via Weinhold's method [21] by permitting better determinations of lower bounds to overlap through the use of Weinberger's formula for overlap [22] which uses the higher roots of the secular determinant. We intend to explore this in a future publication [23].

Finally, for the 5 ^1P state, our result is better than the best previous calcula-tions for this state, the 560-term Accad, Pekeris, and Schiff [24] calculation listed as exact in Table I and the calculation of Green et al. [25]. It also agrees nicely with the estimate of -2.02004 ± 0.00038 a.u. by Wang and Weinhold [26].

2. H^- ^1P. There are no known bound ^1P excited states of H^-. This leads to a photoabsorption spectrum of the negative hydrogen ion which is completely continuous.* However, since the photoabsorption spectrum of the negative hydrogen ion can be imaged by a Stieltjes procedure [28] employing as square-integrable basis functions the pseudostates which are solutions of the ^1P eigen-value problem, we have sought to obtain wave functions for the negative hydrogen ion by the same procedure as was used for the ^1P state for He. Thus, for our initial basis orbitals we chose the STO basis sets ns, mp, $n = 1, 2, 3$, $m = 2, 3, \ldots, 8$. Since split-shell calculations of H^- show the inner electron to be practically unscreened, while the outer one is screened approximately 70% [29], we chose for our orbital exponents $\xi_{ns} = 1.0$, $\xi_{mp} = 0.3$. Taking terms obtained from $ns\,mp\,r_{12}^v$, $v = 0, 1, 2$, leads to the 58-term wave function listed in Table II. Addition of the $9P$ orbital and terms obtained from it leads to the 72-term result. Next, to improve the flexibility of our orbital basis, we added $4s$, $5s$, and $6s$ orbitals and orbitals

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* The continuous photoabsorption spectrum is due to there being no bound ^1P state which can be excited from the ground by an electric dipole transition. There is theoretical evidence, however, for the existence of a bound ^3P state. For example, see Ref. [27].

chosen as fractions of 0.6, i.e., $\xi_p = 0.2$, $\xi_{p'} = 0.15$, $\xi_{p''} = 0.12$. Taking terms derived from the addition of these orbitals to the basis sets already chosen led to the 88- and 108-term results listed in Table II. Further addition of basis orbitals

TABLE II.   Energies E (a.u.) for various expansion length $H^{-1} P$ wave-functions.

Number of terms	State			
	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
58	−0.497995971	−0.493749826	−0.486436398	−0.474472568
72	−0.498342005	−0.494873043	−0.489033322	−0.479805577
88	−0.499122187	−0.497303946	−0.494299250	−0.489699908
108	−0.499183219	−0.497521812	−0.494920486	−0.491402167
109	−0.499183219	−0.497521812	−0.494920486	−0.491402167

and terms did not appreciably change the 108-term results, so we accepted the 108-term wave function as suitable for providing pseudostates for Stieltjes imaging of the negative hydrogen ion photoabsorption spectrum. The 109-term wave function contains an additional term corresponding to the $H^-\,^1S$ wave function (to be discussed later) $\times Y_1^0(\theta_2, \varphi_2)$, in order to improve the oscillator-strength sums $S(k)$ obtainable in the H^- Stieltjes-imaging calculations.* Note that our final results do not indicate a bound ^1P state for H^-.†

B. ^1S States

For ^1S states, the space part of our trial wave functions were again of the form of Eq. (8):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_K C_K \Phi_K(\mathbf{r}_1, \mathbf{r}_2) \tag{8}$$

But the basis functions Φ_K are now specifically of the form

$$\Phi_K(\mathbf{r}_1, \mathbf{r}_2) = (1 + P_{12})/\sqrt{D_{KL}}\, r_1^{n_{K1}-1} r_2^{n_{K2}-1}\, e^{-\xi_{K1} r_1 - \xi_{K2} r_2}$$

$$\times \sum_m Y_{Kl}^{Km*}(\theta_1, \varphi_1)\, Y_{Kl}^{Km}(\theta_2, \varphi_2) \tag{10}$$

suitable to describe a ^1S state.‡

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    * Stieltjes imaging calculations for H^- employing as basis functions the eigenvectors obtained from the 109-term calculation have been described by C. T. Corcoran, D. J. Margoliash, J. S. Sims, S. R. Langhoff, and P. W. Langhoff in a paper presented at the Eighth Midwest Theoretical Chemistry Conference, Madison, Wisconsin, 1974.

    † In the case of $Z = 1$ a state is bound if the energy eigenvalue is less than −0.5 a.u.

    ‡ The symmetry species of each orbital is labeled by l, the degeneracy by D_l, and the subspecies by m. Summing over m from $-l$ to $+l$ then yields the S state appropriate for each state. Notice that this construction is equivalent to applying the projection operator $O(L^2)$ to, for example, the $m = 0$ term in the sum over m.

1. $H^-\ {}^1S$. For our initial $H^-\ {}^1S$ calculations we chose as basis orbitals $1s$, $2s$, $3s$, $4s$, $1s'$, $2s'$, $3s'$, $2p$, $3p$, where the orbital exponents $\xi_s = 0.3$, $\xi_{s'} = 1.05$, $\xi_p = 0.96$, were taken from the configuration interaction calculations of Weiss [30]. Taking terms arising from among the many possible that can be formed from the s, s' basis orbitals times r_{12}^v, $v = 0$, 1, 2, and terms that can be formed from the p basis orbitals times r_{12}^v leads to the 60-, 74, and 92-terms results of Table III. Notice that the results are already energetically rather good at this point, with the 74-term results surpassing the Pekeris [31] 125-term ground-state and 203-term first-excited-state calculations. Since we were interested in obtaining an energetically very good wave-function for the $H^-\ {}^1S$ wave-function to use in Stieltjes-imaging calculations of the H^- photoabsorption spectrum, we added a $4s'$, $5s$, and $4p$ orbital to our basis set and obtained the 100-, 109-, 118-, 127-, 138-, and 148-term results listed in Table III. At this point we felt we had a rather compact

TABLE III.   Energies E(a.u.) for various expansion length $H^-\ {}^1S$ wave-functions.

Number of terms	State			
	$1\ {}^1S$	$2\ {}^1S$	$3\ {}^1S$	$4\ {}^1S$
This work				
60	−0.527750557	−0.494286663	−0.475476565	−0.436569364
74	−0.527750263	−0.495900203	−0.482033841	−0.453509260
92	−0.527750812	−0.497187954	−0.487800371	−0.468677294
100	−0.527750882	−0.497263894	−0.488109593	−0.469377006
109	−0.527750923	−0.497433970	−0.488985842	−0.472158306
118	−0.527750943	−0.497475983	−0.489187265	−0.472839968
127	−0.527750954	−0.497521554	−0.489425358	−0.473652693
148	−0.527750962	−0.498141518	−0.492123023	−0.480517739
Pekeris [31]				
125	−0.527750610	−0.491720		
203	−0.527750936	−0.494517		
308	−0.527750991			
Exact [30]				
	−0.527751014	−0.4981		

$H^-\ {}^1S$ ground-state wave-function of good quality energetically. An interesting sidelight to these calculations is the $2\ {}^1S$ result (-0.49814 a.u.) which is slightly lower than the extrapolated value of Pekeris and still shows no evidence for a bound $2\ {}^1S$ state.

2. $He\ {}^1S$. In this section we consider an attempt to obtain not only a wave-function for the He ^1S ground-state of good quality, but also, within the same basis, good representations for the first three excited states of ^1S symmetry as well. These calculations are very much in the spirit of the He ^1P wave-function

calculations of Section 3.A.1, previous Li calculations we have made [7], and the Li excited S-state calculations of Larsson [2].

First, for the ground-state wave-function we began with basis orbitals $1s$, $2s'$, $3s'$, $2p$, and $3p$, where the orbital exponents $\xi_s = 1.55$, $\xi_{s'} = 2.15$, $\xi_p = 2.67$ were taken from the work of Grein and Tseng [32]. Taking all configurations formed from the sets $\{1s, 2s', 3s'\}+\{2p, 3p\}$ times $\{1, r_{12}, r_{12}^2\}$ led to an energy of -2.90367. Next we added a $2s$ orbital, which yielded an energy of 2.9037229 for 39 configurations. Expanding the basis sets to $1s$–$4s$, $1s'$–$3s'$, $2p$, and $3p$ led to a 60-term ^1S ground-state eigenfunction* for atomic helium with an energy of -2.90372399 a.u. At this point we shifted our emphasis to excited states. Since $e^{-1.55r}$ is a good $1s$ orbital, we chose orbital exponents as fractions of 1.55, i.e., we chose $\xi_{s''} = 1.55/2 = 0.78$, $\xi_{s'''} = 0.52$, $\xi_s^{iv} = 0.35$ as exponents for $m''s''$, $M'''s'''$, $M^{iv}s^{iv}$ orbitals to improve the description of (primarily) the excited ^1S states. Adding terms with these exponents caused linear dependency problems, so we attempted to cut back our ground-state orbital basis set without seriously degrading the ground-state energy. Using $1s$, $2s'$, $3s'$, $2s$, $2p$, and $3p$ led to the 51-term results listed in Table IV. Next we added $1s''$, $2s''$, and $3s''$ orbitals ($\xi_{s''} = 0.78$). This led to the 63-term results in Table IV. To further improve the $2\,^1S$ state as well as to significantly improve the $3\,^1S$ state, we added additional configurations from $\xi_{s''} = 0.78$ and then added orbitals derived from $\xi_{s'''} = 1.55/3 = 0.52$.†

Note that the 70-term results give an energy for the $2\,^1S$ state of the same order as the results of Perkins [3] 31-term HY expansion optimized explicitly for the $2\,^1S$ state. In order to further improve the $2\,^1S$ state as well as improve the description of the $3\,^1S$ state, we added additional terms from $\xi_{s''} = 0.78$ and $\xi_{s'''} = 0.52$. We also added orbitals derived from $\xi_s^{iv} = 1.55/4 = 0.39$. This resulted in the 108-term results listed in Table IV. At this point the energy of the $2\,^1S$ state is better than the 137-term HY expansion of Anderson and Weinhold [20], optimized specifically for the $2\,^1S$ state, and is energetically better than the 308-term Pekeris [31] wave function. We next added more terms derived from $\xi_s^{iv} = 0.39$ to further improve the $3\,^1S$ state, and added additional orbitals derived from $\xi_v = 1.55/5 = 0.31$. Our final 120-term wave function gives the $1\,^1S$, $2\,^1S$, $3\,^1S$, and $4\,^1S$ states with errors of 2×10^{-7}, 6×10^{-8}, 6×10^{-7}, and 3×10^{-5}, respectively, all in the same 120-term basis.

4. Other He ^1S Calculations

Several years ago Green et al. [25] decomposed the energy obtained with the three-term wave function of Chandrasekhar (Ψ_{Ch}) [29] and the famous $3-(\Psi_{3HY})$ and $6-(\Psi_{6HY})$ term wave functions of Hylleraas [35] into s, p, d, contributions ϵ_l. Bunge [36] normalized these contributions and compared them with his estimated "exact" s, p, d, limit contributions. Bunge's results are reproduced in Table V. As

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* This is the $^1S_0^c$ wave-function employed in the calculations of Ref. [11].

† Note that Perkins [3] optimized a s'' orbital in a $2\,^1S$ wave-function calculation and found $s'' = 0.575$. Thus, our methods for estimating good exponents give good agreement with the more systematic procedure of Perkins.

TABLE IV.   Energies E(a.u.) for various expansion length He ^1S wave-functions.

Number of terms	State			
	$1\,^1S$	$2\,^1S$	$3\,^1S$	$4\,^1S$
This work				
51	−2.90372388	−2.12890084	−1.82694862	−1.26331582
63	−2.90372394	−2.14469600	−1.99261939	−1.71311166
70	−2.90372403	−2.14595964	−2.05603897	−1.96205177
108	−2.90372414	−2.14597389	−2.06122512	−2.03270551
113	−2.90372414	−2.14597389	−2.06126385	−2.03333576
120	−2.90372414	−2.14597398	−2.06127116	−2.03355727
Perkins [3]				
11		−2.1458884	−2.0611406	
31		−2.14596	−2.0612621	
		$(\xi_{S'''} = 0.575)$	$(\xi_{S^{iv}} = 0.35)$	
Anderson and Weinhold [20]				
	−2.9037243662	−2.1459736783	−2.0612702515	
Pekeris [31, 34]				
203		−2.145958989		
308		−2.145972779		
444	−2.903724356	−2.145973945		
Extrapolated				
	−2.903724376	−2.145974044	−2.061270530	−2.033584701
Exact				
	−2.903724376 [24]	−2.145974044 [31]	−2.06127177 [33]	−2.033584701 [34]

pointed out by Bunge [36], the implications of the results are remarkable. If we add the sp limit energy error of $\Psi_{6HY}(-0.00048)$ to the total energy for Ψ_{6HY}, we get the exact energy! This implies that Ψ_{6HY} gives the $f,\ g,\ h, \ldots \infty$ energy contributions with more than 6 digits of accuracy, so that all the energy error (to 10^{-6} a.u.) is due to an inadequate representation of the sp basis. Thus, Bunge conjectured that one should be able to compute He wave functions with energy errors smaller than 10^{-6} a.u. just by adding a suitable sp to the 6-dimensional set which defines Ψ_{6HY}, or even better, by using the direct product of both sets as basis. A similar reasoning on Ψ_{Ch},

$$\Psi_{Ch} = N(e^{-Z_1 r_1}\,e^{-Z_2 r_2} + e^{-Z_2 r_1}\,e^{-Z_1 r_2})(1 + \alpha r_{12}) \tag{11}$$

led Bunge to predict that the admixture of a $(1 + \alpha r_{12})$ factor into an sp basis should bring the energy of He to a value in error by no more than 0.00019 a.u. While we have reservations about extrapolating the successes of calculations on helium to other atomic systems, we nevertheless were interested in seeing just

TABLE V.   Energy analysis of interparticle coordinates wave-functions for He.

l	$-\epsilon_l(\Psi_{Ch})$	Error	$-\epsilon_l(\Psi_{3HY})$	Error	$-\epsilon_l(\Psi_{6HY})$	Error	$-\epsilon_l^a$
0	2.87757	0.00146	2.87828	0.00074	2.87867	0.00036	2.879028[b]
1	0.02087	0.00062	0.02117	0.00032	0.02136	0.00013	0.021492[b]
2	0.00209	0.00016	0.00208	0.00017	0.00225	0.00000	0.002254[b]
3	0.00051	0.00004	0.00051	0.00004	0.00055[b]	—	—
Sum 4 to ∞	0.00038	0.00001	0.00039	0.00000	0.00039[b]	—	—
Calc. energy	-2.90142		-2.90244				

[a] Obtained from the data of Table 6, Ref. [36].
[b] These values are considered to be "exact".

how well various s, p, d, f, and r_{12}^v, $v = 0, 1, 2$, bases represented the two-electron helium problem.

Support for Bunge's predictions has been offered by Grein and Tseng [32], who performed variational calculations with correlation factor wave-functions of the type

$$\Psi^\alpha = (1 + \alpha r_{12})\Psi^0 = (1 + \alpha r_{12}) \sum_K C_K \Phi_K^0 \qquad (12)$$

where the Φ_K^0 are configurations in the conventional CI sense and $(1 + \alpha r_{12})$ is an overall correlation factor for the entire wave function. Using a Ψ^0 which is based on Weiss's 35-configuration wave function [30]

$$\Psi^0 = \{1s, 2s, 1s', 2s', 3s'\} + \{2p, 3p, 2p', 3p'\} \qquad (13)$$

Grein and Tseng [32] obtained the results listed in Table II for 15- and 25-configuration expansions. The notation in Eq. (13) and Table VI is such that all

TABLE VI.   Ground-state energy (a.u.) of the helium atom for various $\{s, p\}\{1, r_{12}, r_{12}^2\}$ sets.[a]

K	$\Psi^0(K)$	α_{opt}	$E^0(K)$	$E^\alpha(K)$	E
15	$\{1s, 2s, 1s', 2s', 3s'\}$	0.28	-2.878955	-2.902404	$(-2.903474)^b$
25	$\Psi^0(15) + \{2p, 3p, 2p', 3p'\}$	0.39	-2.900390	-2.903559	
50	$\Psi^0(25) \times \{1, r_{12}\}$				-2.903712
75	$\Psi^0(25) \times \{1, r_{12}, r_{12}^2\}$				-2.903722

[a] Orbital exponents $\xi_s = 1.48$, $\xi_s = 3.7$, $\xi_p = 2.7$, $\xi_{p'} = 5.4$.
[b] This result is for the 15-term $\Psi^0(K) \times \{1, r_{12}\} = 30$-term wave-function of Table VII.

possible configurations are formed of the orbitals collected within the same brackets. The orbital exponents were taken from Weiss's 35-configuration wave function [30]. The energies E^0 and E^α refer to $\Psi^0(K)$ and $\Psi^\alpha = (1 + \alpha r_{12}) \Psi^0(K)$, respectively. We have recomputed the results of Grein and Tseng, obtaining complete agreement with their results.* Note that the 25-term results conform to Bunge's [36] prediction that "the admixture of a $(1 + \alpha r_{12})$ factor into an sp basis should bring the energy of He to a value in error by no more than 0.00019 a.u." Grein and Tseng's value is in error by 0.00016 a.u.!

Grein and Tseng [32], like others [37, 38] approach the solution of the Schrodinger equation $\mathcal{H}\Psi = E\Psi$, where $\mathcal{H}$ is given by Eq. (1), by attempting to combine a correlation factor with the more systematic approach of the CI method. In the contrast to these attempts to use an average factor for the whole atom (correlation factor), our approach [6, 7, 8] permits the utilization of a pair correlation factor r_{ij} in those configurations which make the greatest contribution

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* In Table I or Ref. [38] we obtained -2.87855 a.u. for $E_1^0(6)$ rather than the listed -2.85855. This misprint has been confirmed by F. Grein (personal communication).

in a CI expansion, and allows for freely varying coefficients for r_{ij}'s with different configurations Φ_K. In order to get some idea of the constraint involved in using a correlation factor approach, as well as to allow the direct projection of the $\Psi^0(25)$ sp basis times the $\{1, r_{12}\}$ basis of the 25-term $\Psi^\alpha(25)$ calculation to obtain its maximal value (energetically), we did a 50-term calculation consisting of $\Psi^0(25)$ and $r_{12}\Psi^0(25)$, with freely varying coefficients. The results are presented in Table VI, where we note that the direct product of a suitable sp basis times $\{1, r_{12}\}$ gives an energy value for He in error by 0.000012 a.u.! To get an idea of how well the direct product of a suitable sp basis times $\{1, r_{12}, r_{12}^2\}$ would do, we also added 25 terms corresponding to $r_{12}^2\Psi^0(25)$ and did the 75-term calculation reported in Table VI. The energy error is 2×10^{-6} a.u., which is indeed indicative of the potential accuracy of an sp STO, r_{12}^v, $v = 0, 1, 2$ basis. Our best results for this type of basis were reported in Section 3.B.2 and in Table VII, which shows the basis capable of producing He wave functions with energy errors smaller than 10^{-7} a.u.; this is even better than Bunge's predictions.

TABLE VIII. Ground-state energy (a.u.) of the helium atom for various $\{s, p, d\}$
$\{1, r_{12}\}$ sets.
$S = \{1s, 2s, 1s', 2s', 3s'\}$ $S' = \{S + 3s, 4s'\}$ $S'' = \{S' + 4s\}$

Number of terms		E
30	$S \times \{1, r_{12}\} =$	-2.9034739
56	$S' \times \{1, r_{12}\} =$	-2.9034944
72	$S'' \times \{1, r_{12}\} =$	-2.9034952
	$P = \{2p, 3p, 2p', 3p'\}$	
76	$\{S' + P\}\{1, r_{12}\} =$	-2.90372404
	$D = \{3d, 4d, 5d\}$	
88	$\{S' + P + D\}\{1, r_{12}\} =$	-2.90372424

If the direct produce of an sp STO, r_{12}^v, $v = 0, 1, 2$ basis is capable of producing He wave functions with energy errors smaller than 10^{-7} a.u., then so is the direct product of an spd STO, r_{12}^v, $v = 0, 1$ basis. Since replacing the r_{12}^2 terms with d type STO's leads to wave functions more closely resembling conventional CI wave functions, and hopefully can lead to more efficient computer codes, we carried out the $\{spd\}\{1, r_{12}\}$ calculations listed in Table VII. The notation on the terms is the same as for Table II and the orbital exponents are again taken from Weiss [30]. The final result is noteworthy in that an energy in error by 1.3×10^{-7} a.u. can be obtained in a very straightforward manner, utilizing a suitable $\{spd\}\{1, r_{12}\}$ basis.

5. Conclusions

Combined CI-HY techniques have proven useful in obtaining the ground and first three excited two-electron S states with an error on the order of 10^{-7} a.u. within the same 120-term basis, and in obtaining the four lowest He ^1P states, all

with an error $\leq 2 \times 10^{-6}$ a.u. H^- ^1S and ^1P states are also treated by the same procedure. The H^- calculations and the He $5\ ^1P$ result are better than previous results reported in the literature. There are indications that an *spd* STO, r_{ij}^v, $v = 0, 1$ basis might be an excellent one for states of first-row atoms. Work is currently in progress to use some of the wave functions reported herein to compute $n\ ^1S \to m\ ^1P$ transition probabilities, along with upper and lower bounds,* as well as electric polarizabilities, with rigorous lower bounds,† for Stieltjes imaging of photodispersion profiles of He and H^-.‡

Acknowledgment

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* Similar calculations for beryllium are reported in Ref. [9].

† Similar calculations for beryllium are reported in Ref. [10].

‡ Calculations have already been done for He (see Ref. [11]) and a preliminary report of the H^- calculations has been made (see Ref. [33]).

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