

The value of the $\langle z_a | \nabla | S_a \rangle$ contribution to the matrix element of ∇ is based on the experimental value of 0.09 for the carbon $2s \rightarrow 2p$ oscillator strength.

Fortunately we do not need to find accurate values for (A13) or (A14), provided one or both are small. We have evaluated these with two sets of coefficients γ_s , γ_{Hx} and γ_x ; one set simply takes

$$\gamma_s = \gamma_x = \gamma_{Hx} = (3)^{-1/2}.$$

The second set was that of the SCF calculation of

Palke and Lipscomb,³² namely

$$\gamma_s = 0.721, \quad \gamma_x = 0.421, \quad \gamma_{Hx} = 0.550.$$

A calculation was also performed for the unrealistic assumption that $\langle z_a | \nabla | S_a \rangle = 0$, but this led to far too large oscillator strengths for the $\pi_z \rightarrow \sigma^*$ transition (> 0.1). Even with this assumption, the rotational strength of the $\pi_z \rightarrow \sigma^*$ remained of order $1-4 \times 10^{-40}$ cgs, far too small to contribute noticeably to the cd curve.

³² W. E. Palke and W. Lipscomb, *J. Am. Chem. Soc.* **88**, 2384 (1966).

Some Aspects of Electron Correlation in Open-Shell States. 2^1P and 2^3P Helium*

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Accurate wavefunctions for the 2^3P and 2^1P states of helium have been analyzed into pair, polarization, and semi-internal correlation effects. The dynamical, transferable pair-correlation energies account for approximately 90% of the total correlation energies. The special open-shell effects, symmetry polarizations, and semi-internal correlation, account for half the remaining correlation energy. It is shown computationally that the polarization and semi-internal correlation energies can be computed separately from the pair energies to about 96% accuracy.

I. INTRODUCTION

In closed-shell states of atoms and molecules the main electron correlation effect is pair correlation.¹⁻⁶ Open-shell states are characterized by three additional physically important correlation effects⁷⁻⁹: internal correlation, in which no electrons leave the Hartree-Fock sea; semi-internal correlation, in which one electron leaves the Hartree-Fock sea and a second moves from an occupied to a vacant spin orbital in the sea; and polarizations, which are one-electron excitations out of the sea which tend to make the spatial parts of doubly occupied orbitals different or which tend to break the spatial symmetry of an orbital. Pair correlations, to a high degree of accuracy, can be computed independently

of one another,^{1-6, 10-15} and dynamical pair-correlation energies are relatively invariant from atom to atom.¹⁻⁶ It has been suggested^{7-9, 16} that the specifically open-shell correlation effects can be computed independently from the pair-correlation effects, but there are not yet extensive numerical results which gauge the accuracy lost by calculating the open-shell effects separately. Moreover, the open-shell correlation effects are strongly subject to "exclusion effects" which change from atom to atom.

Our purpose here is to analyze an accurate wavefunction for two simple atomic states, 2^1P and 2^3P , which comprise the $1s2p$ configuration of helium, into the various physically meaningful correlation effects as formulated in Refs. 7-9. The relative magnitudes of the various effects are compared, and the loss of accuracy of computing some of the effects "separately" is assessed. This study is the first analysis of an accurate

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¹ O. Sinanoğlu, *J. Chem. Phys.* **36**, 706 (1962).

² O. Sinanoğlu, *J. Chem. Phys.* **36**, 3198 (1962).

³ O. Sinanoğlu and D. F. Tuan, *J. Chem. Phys.* **38**, 1740 (1963).

⁴ D. F. Tuan and O. Sinanoğlu, *J. Chem. Phys.* **41**, 2677 (1964).

⁵ V. McKoy and O. Sinanoğlu, *J. Chem. Phys.* **41**, 2689 (1964).

⁶ O. Sinanoğlu, *Advan Chem Phys.* **6**, 315 (1964).

⁷ H. J. Silverstone and O. Sinanoğlu, *J. Chem. Phys.* **44**, 1899 (1966).

⁸ H. J. Silverstone and O. Sinanoğlu, *J. Chem. Phys.* **44**, 3608 (1966).

⁹ H. J. Silverstone and O. Sinanoğlu, in *Modern Quantum Chemistry—Istanbul Lectures*, O. Sinanoğlu, Ed. (Academic Press Inc., New York, 1965), Pt. 2.

¹⁰ References 11-15 are given as examples and are not meant to exhaust the many recent accurate calculations which have grown out of the theory developed in Refs. 1 and 2.

¹¹ H. P. Kelly, *Phys. Rev.* **131**, 684 (1963).

¹² H. P. Kelly, *Phys. Rev.* **136**, B896 (1964).

¹³ R. K. Nesbet, *Phys. Rev.* **155**, 51, 56 (1967).

¹⁴ A. W. Weiss, *Phys. Rev.* **162**, 71 (1967).

¹⁵ H. F. Schafer III and F. E. Harris, *Phys. Rev.* **167**, 67 (1968).

¹⁶ See also, H. J. Silverstone, and O. Sinanoğlu, *J. Chem. Phys.* **46**, 854 (1967).

open-shell wavefunction from the viewpoint developed in Refs. 7-9.

II. WAVEFUNCTION

A. Choice of Exact Wavefunction and Hartree-Fock Wavefunction

To analyze electron correlation we need an exact wavefunction and a Hartree-Fock wavefunction. There are several accurate calculations of the 2^1P and 2^3P wavefunctions reported in the literature.¹⁷⁻²⁰ The ones analyzed here were obtained by Green, Kolchin, and Johnson¹⁸ (GKJ). Other wavefunctions are more accurate but usually involve explicit functions of r_{12} . The GKJ ψ is constructed from Slater-type atomic orbitals (STO), is cast in configuration-interaction (CI) form, and is consequently particularly convenient for us to work with. A comparison of various calculated energies for $1s2p$ He is given in Table I.

The restricted Hartree-Fock (RHF) wavefunctions, ϕ_{RHF} , for $2^{1,3}P$ He have been accurately calculated by Davidson.²¹ His basis functions, however, are considerably different from those of GKJ. To reduce computing time in our analysis, we found it convenient to recalculate ϕ_{RHF} in a basis selected from GKJ. The corresponding RHF energy does not differ significantly from Davidson's (cf. Table I, lines B and C).

B. Correlation Effects in the Exact Wavefunction

The starting point for a discussion of electron correlation in $SS^{7-9,22}$ was taken as the "general restricted Hartree-Fock" (GRHF) wavefunction. Here GRHF means the linear combination of Slater determinants, composed only of $1s$ and $2p$ orbitals, which gives a lower expectation value of the energy than any other approximate wavefunction having the same form. There are, however, precisely one odd-parity $1P$ and one odd-parity $3P$ two-electron wavefunctions with given M_L and M_S quantum numbers that can be made from $1s$ and $2p$ orbitals, the ϕ_{RHF} . So here GRHF and RHF mean the same thing. Moreover, no internal correlation effects⁷⁻⁹ are possible.

We now write the $2^{1,3}P$ wavefunctions for He in the notation of SS. The $1s$ and $2p$ denote the appropriate RHF orbitals, α and β the usual spin functions, \mathcal{A} the antisymmetrization operator, and ψ the exact wavefunction. Then, following Eqs. (1)-(4) of SS,⁸ one can

TABLE I. Experimental and some computed energies for 2^3P and 2^1P helium.

	Total energy (a.u.) ^a		Comment
	2^3P	2^1P	
A	-2.133285	-2.123953	Experimental ^b
B	-2.131433	-2.122460	Hartree-Fock (Davidson) ^c
C	-2.131432	-2.122460	Hartree-Fock (this work) ^d
D	-2.133164	-2.123843	Exact nonrelativistic (SLPR) ^e
E	-2.133128	-2.123782	Used in this work as exact value (GKJ) ^f
F	-2.133164		Schwartz ^g
G	-2.13316	-2.12384	Weiss ^h
Correlation energy			
H	-0.001731 (-0.04710 eV)	-0.001383 (-0.03763 eV)	True correlation energy, (D-B)
I	-0.001696 (-0.04614 eV)	-0.001322 (-0.03597 eV)	Correlation energy, as used in this work (E-C)

^a 1 a.u. = 219 444.528 cm⁻¹ = 27.207 eV for He⁺.

^b C. E. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467, 1, 3 (1949). The center of gravity of the $3P$ multiplet is listed here.

^c Reference 21.

^d The Hartree-Fock wavefunctions used in this work were computed in a basis of $4s$ orbitals and $7p$ orbitals coinciding with the 11 basis functions of the $nsn'p$ configurations of GKJ, Ref. 18.

^e Reference 17.

^f Reference 18. This is the only calculation reported of configuration interaction with Slater-type atomic orbitals.

^g Reference 19.

^h Reference 20.

write for the ($M_L=0$, $M_S=S$) states,

$$\psi = \phi_{\text{RHF}} + \chi, \quad (1)$$

$$\langle \phi_{\text{RHF}} | \phi_{\text{RHF}} \rangle = 1, \quad (2)$$

$$\langle \phi_{\text{RHF}} | \chi \rangle = 0, \quad (3)$$

$$\phi_{\text{RHF}}(2^3P) = \mathcal{A}1s\alpha 2p_0\alpha, \quad (4)$$

$$\phi_{\text{RHF}}(2^1P) = 2^{-1/2}\mathcal{A}(1s\alpha 2p_0\beta + 2p_0\alpha 1s\beta), \quad (5)$$

$$\begin{aligned} \chi(2^3P) = & \mathcal{A}(1s\alpha\hat{f}_{2p_0\alpha}^{(P)} + \hat{f}_{1s\alpha}^{(P)} 2p_0\alpha \\ & + 2p_+\alpha\hat{f}_{1s\alpha,2p_0\alpha;2p_+\alpha} + 2p_-\alpha\hat{f}_{1s\alpha,2p_0\alpha;2p_-\alpha} \\ & + 2^{-1/2}\mathcal{A}1s\alpha 2p_0\alpha + 1s\alpha\hat{f}_{2p_0\alpha}^{(\text{eoc})} + \hat{f}_{1s\alpha}^{(\text{eoc})} 2p_0\alpha). \end{aligned} \quad (6)$$

$$\begin{aligned} \chi(2^1P) = & 2^{-1/2}\mathcal{A}(1s\alpha\hat{f}_{2p_0\beta}^{(P)} + \hat{f}_{1s\alpha}^{(P)} 2p_0\beta \\ & + \hat{f}_{2p_0\alpha}^{(P)} 1s\beta + 2p_0\alpha\hat{f}_{1s\beta}^{(P)} + 1s\alpha\hat{f}_{2p_0\beta}^{(\text{eoc})} \\ & + \hat{f}_{1s\alpha}^{(\text{eoc})} 2p_0\beta + \hat{f}_{2p_0\alpha}^{(\text{eoc})} 1s\beta + 2p_0\alpha\hat{f}_{1s\beta}^{(\text{eoc})} \\ & + 2p_+\alpha\hat{f}_{1s\alpha,2p_0\beta;2p_+\alpha} + 2p_-\alpha\hat{f}_{1s\alpha,2p_0\beta;2p_-\alpha} + 2p_0\alpha\hat{f}_{1s\alpha,2p_0\beta;2p_0\alpha} \\ & + 2p_+\beta\hat{f}_{1s\alpha,2p_0\beta;2p_+\beta} + 2p_-\beta\hat{f}_{1s\alpha,2p_0\beta;2p_-\beta} + 2p_+\alpha\hat{f}_{2p_0\alpha,1s\beta;2p_+\alpha} \\ & + 2p_-\alpha\hat{f}_{2p_0\alpha,1s\beta;2p_-\alpha} + 2p_+\beta\hat{f}_{2p_0\alpha,1s\beta;2p_+\beta} + 2p_-\beta\hat{f}_{2p_0\alpha,1s\beta;2p_-\beta} \\ & + 2p_0\beta\hat{f}_{2p_0\alpha,1s\beta;2p_0\beta} + 2^{-1/2}\mathcal{A}1s\alpha,2p_0\beta + 2^{-1/2}\mathcal{A}2p_0\alpha,1s\beta). \end{aligned} \quad (7)$$

¹⁷ B. Schiff, H. Lifson, C. L. Pekeris, and P. Rabinowitz, Phys. Rev. A140, 1104 (1965).

¹⁸ L. C. Green, E. K. Kolchin, and N. C. Johnson, Phys. Rev. 139A, 373 (1965).

¹⁹ C. Schwartz, Phys. Rev. 134A, 1181 (1964).

²⁰ A. W. Weiss, J. Res. Natl. Bur. Std. 71A, 163 (1967).

²¹ E. R. Davidson, J. Chem. Phys. 41, 656 (1964), and J. Chem. Phys. 42, 4199 (1965).

²² SS is used from here on to denote Refs. 7-9.

Equations (6) and (7) are simplified below. Briefly, $f_i^{(P)}$ denotes a (one-electron) polarization, $\hat{f}_{ij;k}$ a semi-internal correlation function, and \hat{u}_{ij} an antisymmetric pair correlation function. One new symbol, $\hat{f}_i^{(\text{eoc})}$, has been introduced to represent small one-electron effects deliberately omitted from the approximate χ formulated in SS, but which are identical in nature to the \hat{f}_i in the closed-shell case, and which may be regarded as arising from the "effect of correlation on orbitals." The carat on the \hat{f} 's and \hat{u} 's denotes one-electron orthogonality to all eight spin-orbitals of the RHF sea [$\equiv (1s\alpha, 1s\beta, 2p_+\alpha, 2p_+\beta, 2p_0\alpha, 2p_0\beta, 2p_-\alpha, 2p_-\beta)$], e.g.,

$$\langle 1s\alpha | \hat{f}_{1s\alpha}^{(P)} \rangle = 0, \quad (8)$$

$$\langle 2p_0\alpha | \hat{f}_{1s\alpha, 2p_0\alpha; 2p_+\alpha} \rangle = 0, \quad (9)$$

$$\int dV_1 [2p_+\alpha(1)]^* \hat{u}_{1s\alpha 2p_0\alpha}(1, 2) = 0, \quad (10)$$

etc.

C. Simplification of χ

The form of χ in Eqs. (6) and (7), apart from the $f^{(\text{eoc})}$, is what is suggested by perturbation theory.⁷ For present purposes these expressions for χ can be drastically simplified by symmetry.¹⁶

1. Semi-internal Correlations and Polarizations

In CI language, polarization and semi-internal correlations here consist of all Slater determinants orthogonal to ϕ_{RHF} , having precisely one electron in a $1s$ or $2p$ RHF spin orbital, and having a nonzero energy matrix element with ϕ_{RHF} . Via angular-momentum symmetry,¹⁶ and the requirement of a nonvanishing energy matrix element with ϕ_{RHF} , one can conclude that

$$\hat{f}_{2p}^{(P)} \equiv 0, \quad (11)$$

(the field of the $1s$ orbital cannot polarize the $2p$ orbital),

$$\hat{f}_{1s}^{(P)} \text{ has } d \text{ symmetry}, \quad (12)$$

(the $2p$ orbital has a nonspherically symmetric field which induces a d polarization on the $1s$ orbital), and

$$\hat{f}_{1s, 2p_i; 2p_j} \text{ all have } d \text{ symmetry}. \quad (13)$$

Symmetry, in fact, allows one to replace all the polarization and semi-internal correlation terms in each of Eqs. (6) and (7) by expressions involving a single d function each (psi=polarization and semi-internal correlation),

$$\chi_{\text{psi}}(2^3P) = 10^{-1/2} \alpha [2(d_0\alpha)(2p_0\alpha) + \sqrt{3}(2p_+\alpha)(d_-\alpha) + \sqrt{3}(2p_-\alpha)(d_+\alpha)], \quad (14)$$

$$\chi_{\text{psi}}(2^1P) = 20^{-1/2} \alpha \{ 2(d_0\alpha)(2p_0\beta) + 2(2p_0\alpha)(d_0\beta) + \sqrt{3}[(2p_+\alpha)(d_-\beta) + (d_-\alpha)(2p_+\beta) + (2p_-\alpha)(d_-\beta) + (d_+\alpha)(2p_-\beta)] \}. \quad (15)$$

Again Eqs. (14) and (15) hold because of symmetry and the restriction to terms having a nonzero energy matrix element with ϕ_{RHF} .

2. Pair Correlations

The pair-correlation functions represent all double excitations out of the RHF sea. In Eq. (7), only the $1P$ linear combination of $\hat{u}_{1s\alpha 2p_0\beta}$ and $\hat{u}_{2p_0\alpha 1s\beta}$ occurs,

$$\hat{u}_{1s 2p_0}(1P) = 2^{-1/2}(\hat{u}_{1s\alpha 2p_0\beta} + \hat{u}_{2p_0\alpha 1s\beta}). \quad (16)$$

3. Effect of Correlation on Orbitals

The $\hat{f}_i^{(\text{eoc})}$ are the single excitations present in ψ which have a zero-energy matrix element with ϕ_{RHF} . The $\hat{f}_i^{(\text{eoc})}$ here must have the same symmetry properties as spin orbital i , e.g., $\hat{f}_{1s\alpha}^{(\text{eoc})}$ is a s -type function with α spin and $\hat{f}_{1s\beta}^{(\text{eoc})}$ is its β -spin "partner."

The above considerations lead to simpler looking χ 's,

$$\chi(2^3P) = \chi_{\text{psi}}(3P) + \hat{u}_{1s\alpha 2p_0\alpha} + \alpha(1s\alpha \hat{f}_{2p_0\alpha}^{(\text{eoc})} + \hat{f}_{1s\alpha}^{(\text{eoc})} 2p_0\alpha), \quad (17)$$

$$\chi(2^1P) = \chi_{\text{psi}}(1P) + \hat{u}_{1s 2p_0}(1P) + 2^{-1/2} \alpha (1s\alpha \hat{f}_{2p_0\beta}^{(\text{eoc})} + \hat{f}_{2p_0\alpha}^{(\text{eoc})} 1s\beta + \hat{f}_{1s\alpha}^{(\text{eoc})} 2p_0\beta + 2p_0\alpha \hat{f}_{1s\beta}^{(\text{eoc})}). \quad (18)$$

III. PARTITION OF THE ENERGY

Let H denote the nonrelativistic electronic Hamiltonian, E the exact energy, E_{RHF} the RHF energy, and E_{corr} the correlation energy. From Eqs. (1)–(3) and the Schrödinger equation, one can write

$$H\psi = E\psi, \quad (19)$$

$$E = E_{\text{RHF}} + E_{\text{corr}}, \quad (20)$$

$$E_{\text{RHF}} = \langle \phi_{\text{RHF}} | H | \phi_{\text{RHF}} \rangle, \quad (21)$$

$$E_{\text{corr}} = \langle \phi_{\text{RHF}} | H | \chi \rangle, \quad (22)$$

$$= \langle \phi_{\text{RHF}} + \chi | H - E_{\text{RHF}} | \phi_{\text{RHF}} + \chi \rangle / (1 + \langle \chi | \chi \rangle). \quad (23)$$

In this section we discuss the partitioning of E_{corr} into the individual correlation energies for the various correlation processes in χ , Eqs. (6), (7), (14), (15), (17), and (18).

The cleanest partition of E_{corr} into physically meaningful terms follows directly from Eq. (22), which has the same form as the second-order energy expression [Eq. (50) of SS⁷]. For 2^3P ,

$$E_{\text{corr}}(2^3P) = \varepsilon_{1s\alpha}^{(P)} + \varepsilon(\text{semi-internal}) + \varepsilon_{1s\alpha 2p_0\alpha}, \quad (24)$$

where [cf. Eqs. (6) and (14)]

$$\varepsilon_{1s\alpha}^{(P)} = [2 / (10)^{1/2}] \langle \phi_{\text{RHF}} | r_{12}^{-1} | d_0\alpha 2p_0\alpha \rangle, \quad (25)$$

$$\varepsilon_{1s\alpha 2p_0\alpha} = \langle \phi_{\text{RHF}} | r_{12}^{-1} | \hat{u}_{1s\alpha 2p_0\alpha} \rangle, \quad (26)$$

\mathcal{E} (semi-internal)

$$= \left(\frac{3}{10}\right)^{1/2} \langle \phi_{\text{RHF}} | r_{12}^{-1} | \mathcal{G}(2p_+\alpha d_-\alpha + 2p_-\alpha d_+\alpha) \rangle, \quad (27)$$

$$= \mathcal{E}_{1s\alpha, 2p_0\alpha; 2p_+\alpha} + \mathcal{E}_{1s\alpha, 2p_0\alpha; 2p_-\alpha}. \quad (28)$$

Note that by symmetry,

$$\mathcal{E}(\text{semi-internal}) = (3/2)\mathcal{E}_{1s\alpha}^{(P)}, \quad (29)$$

$$= 2\mathcal{E}_{1s\alpha, 2p_0; 2p_-\alpha}. \quad (30)$$

The total polarization and semi-internal correlation energy for 2^3P (independent of M_L and M_S) is

$$\mathcal{E}_{\text{psi}} = \mathcal{E}_{1s\alpha}^{(P)} + \mathcal{E}(\text{semi-internal}). \quad (31)$$

A similar breakdown for 2^1P is

$$E_{\text{corr}}(2^1P) = \mathcal{E}_{1s}^{(P)} + \mathcal{E}(\text{semi-internal}) + \mathcal{E}_{1s2p_0}(1P), \quad (32)$$

where

$$\mathcal{E}_{1s2p_0}(1P) = \langle \phi_{\text{RHF}} | r_{12}^{-1} | \hat{u}_{1s2p_0}(1P) \rangle, \quad (33)$$

$$\mathcal{E}_{1s}^{(P)} = 5^{-1/2} \langle \phi_{\text{RHF}} | r_{12}^{-1} | \mathcal{G}(d_0\alpha 2p_0\beta + 2p_0\alpha d_0\beta) \rangle, \quad (34)$$

$$\mathcal{E}(\text{semi-internal}) = (3/2)\mathcal{E}_{1s}^{(P)}, \quad (35)$$

$$\mathcal{E}_{\text{psi}} = \mathcal{E}_{1s}^{(P)} + \mathcal{E}(\text{semi-internal}). \quad (36)$$

Another partition of E_{corr} into physically meaningful terms follows from the variational expression for E_{corr} [Eq. (23)]. One can make maximum use of symmetry by keeping the polarization and semi-internal correlation effects together.²³ Following the spirit of Eqs. (15)–(21) of SS,⁸ we write for 2^3P

$$E_{\text{corr}}(2^3P) = D^{-1}(\tilde{\epsilon}_{1s\alpha 2p_0\alpha} + \tilde{\epsilon}_{\text{psi}} + R). \quad (37)$$

Here,

$$D = 1 + \langle \chi | \chi \rangle, \quad (38)$$

$$\tilde{\epsilon}_{1s\alpha 2p_0\alpha} = 2 \langle \phi_{\text{RHF}} | r_{12}^{-1} | \hat{u}_{1s\alpha 2p_0\alpha} \rangle + \langle \hat{u}_{1s\alpha 2p_0\alpha} | H - E_{\text{RHF}} | \hat{u}_{1s\alpha 2p_0\alpha} \rangle, \quad (39)$$

$$\tilde{\epsilon}_{\text{psi}} = 2 \langle \phi_{\text{RHF}} | r_{12}^{-1} | \chi_{\text{psi}} \rangle + \langle \chi_{\text{psi}} | H - E_{\text{RHF}} | \chi_{\text{psi}} \rangle, \quad (40)$$

and R denotes all the remaining terms, the most important of which are

$$\begin{aligned} & \tilde{\epsilon}[\hat{f}_{2p_0\alpha}^{(\text{occ})}] \\ & \equiv \langle 1s\alpha \hat{f}_{2p_0\alpha}^{(\text{occ})} | H - E_{\text{RHF}} | 1s\alpha \hat{f}_{2p_0\alpha}^{(\text{occ})} - \hat{f}_{2p_0\alpha}^{(\text{occ})} 1s\alpha \rangle, \end{aligned} \quad (41)$$

and

$$\begin{aligned} & \tilde{\epsilon}[\hat{f}_{2p_0\alpha}^{(\text{occ})} \times \hat{u}_{1s\alpha 2p_0\alpha}] \\ & \equiv 2 \langle \hat{u}_{1s\alpha 2p_0\alpha} | H - E_{\text{RHF}} | \mathcal{G}(1s\alpha \hat{f}_{2p_0\alpha}^{(\text{occ})}) \rangle. \end{aligned} \quad (42)$$

Similar expressions hold for the 2^1P case.

In the next section the results of analyzing E_{corr} for GKJ ψ according to Eqs. (24)–(42) are discussed.

²³ Cf. the discussion of lithium in Sec. VII of Ref. 8.

IV. COMPUTATIONS AND DISCUSSION

The extraction of the various one- and two-electron correlation functions from the known ψ is straightforward, following generally the “method of successive partial orthogonalizations.”^{24,7} For the exact ψ 's we chose the 42-term CI ψ 's of GKJ.¹⁸ The ϕ_{RHF} was constructed from the 4s STO's and 7p STO's appearing in the first 22 configurations of GKJ and was very similar to the ϕ_{RHF} reported by Davidson.²¹ The ψ and ϕ_{RHF} were “read in” in single precision, then all subsequent calculations were carried out in double precision on an IBM 7094 computer. All results reported are given to 1×10^{-6} a.u. The numerical accuracy, however, is more likely about 1×10^{-5} a.u. Moreover, the total correlation energies computed with the GKJ ψ are $\sim 5 \times 10^{-5}$ a.u. smaller in magnitude than the most accurate value^{17,25} (see Table I, lines H and I), which is the grain of salt to be included with our conclusions.

A. Magnitudes of the Individual Correlation Effects

The numerical analysis of E_{corr} into individual correlation effects is reported in Table II. Although the total correlation energies of the 2^3P and 2^1P states are rather small, -0.05 and -0.04 eV, respectively (note that the 1s and 2p orbitals are spatially well separated), it is curious that the 2^3P correlation energy is larger than the 2^1P correlation energy (this seems to be true for all $n^1, 3P$ states^{17,18,21}), in apparent violation of the dictum that triplet correlation is always less than singlet correlation energy because of the Fermi hole.

From Table II one sees that roughly 90% of the total correlation energy is accounted for by pair correlation with most of the remainder accounted for by polarization and semi-internal correlation, which here is 3% of the total correlation energy for 2^3P and 10% of the total for 2^1P . Although small in magnitude here, the relative value of the polarization and semi-internal correlation energy is not negligible. (In first row atoms 10% of E_{corr} is not small in magnitude.²⁶) Qualitatively, it matters little whether the energy is partitioned from $\langle \phi_0 | H | \chi \rangle$ [Eq. (22)] or from

$$\langle \phi_0 + \chi | H - E_{\text{RHF}} | \phi_0 + \chi \rangle / (1 + \langle \chi | \chi \rangle)$$

[Eq. (23)], but the $\langle \phi_0 | H | \chi \rangle$ expression does not do justice to the “effects of correlation on orbitals” which do enter χ . It is instructive to note that the contribution to the variational energy from the matrix element between $\hat{f}_{2p}^{(\text{occ})}$ and \hat{u}_{1s2p} [Eq. (42)] is negative and the same order of magnitude as $\tilde{\epsilon}_{\text{psi}}$ but the “direct” matrix

²⁴ O. Sinanoğlu, Rev. Mod. Phys. **35**, 517 (1963).

²⁵ Convenience always exacts its price.

²⁶ In first-row atoms, d polarization of the 2s orbital and $(2s2p; 2p_i)$ -type semi-internal correlation are relatively even more important. See O. Sinanoğlu, I. Öksüz, and B. Skutnik (unpublished), Cf. also, H. J. Silverstone and M. L. Yin, J. Chem. Phys. **49**, 2026 (1968).

TABLE II. Analysis of electron correlation in 2^3P and 2^1P helium.

State	E_{corr}^a	ϵ_{1s2p}^b	$\tilde{\epsilon}_{1s2p}^c$	$\epsilon_{1s}^{(P) d}$	$\epsilon(\text{semi-internal})^e$	ϵ_{psi}^f	$\tilde{\epsilon}_{\text{psi}}^g$
2^3P	-0.001696 a.u. -0.04614 eV	-0.001637 a.u. -0.04453 eV	-0.001598 a.u. -0.04349 eV	-0.000023 a.u. -0.00062 eV	-0.000034 a.u. -0.00093 eV	-0.000057 a.u. -0.00156 eV	-0.000046 a.u. -0.00126 eV
2^1P	-0.001322 a.u. -0.03597 eV	-0.001197 a.u. -0.03257 eV	-0.001155 a.u. -0.03142 eV	-0.000048 a.u. -0.00132 eV	-0.000073 a.u. -0.00197 eV	-0.000121 a.u. -0.00329 eV	-0.000124 a.u. -0.00338 eV
	$\tilde{\epsilon}[\hat{f}_{2p}^{(\text{eco})} \times \hat{u}_{1s2p}]^h$	$[\hat{f}_{2p}^{(\text{eco})}]^i$	$R - [\hat{f}_{2p}^{(\text{eco})} \text{ terms}]$	R^i	D^k	$\langle \hat{u}_{1s2p} \hat{u}_{1s2p} \rangle^l$	$\langle \chi_{\text{psi}} \chi_{\text{psi}} \rangle^m$
2^3P	-0.000063 a.u. -0.00172 eV	+0.000032 a.u. +0.00088 eV	-0.000022 a.u. -0.00061 eV	-0.000053 a.u. -0.00145 eV	1.00095	0.00069	0.00004
2^1P	-0.000062 a.u. -0.00168 eV	+0.000032 a.u. +0.00088 eV	-0.000009 a.u. -0.00026 eV	-0.000039 a.u. -0.00106 eV	1.00071	0.00043	0.00006

^a See Line I, Table I.

^b Equations (26) and (33).

^c Equation (39).

^d Equations (25) and (34).

^e Equations (29) and (35).

^f Equations (31) and (36).

^g Equation (40).

^h Equation (42).

ⁱ Equation (41).

^j Computed explicitly.

^k Equation (38).

^l Equations (17) and (18).

^m Equations (14) and (15).

element [Eq. (41)] is positive, clearly bringing out the "eco" nature of $\hat{f}_{2p}^{(\text{eco})}$. The contribution of $\hat{f}_{1s}^{(\text{eco})}$ was completely negligible.

B. Separate Calculation of Individual Correlation Effects

By separate calculation of a correlation effect we mean the minimization of the variational energy using a wavefunction whose χ has in it only that correlation. Separate calculation of pair correlation functions has already been well justified, and separate calculation of $\hat{f}_i^{(\text{eco})}$ is not possible because the "direct terms" in E_{corr} are positive (cf. $\tilde{\epsilon}[\hat{f}_{2p}^{(\text{eco})}]$ in Table II), so here we concentrate on polarization and semi-internal correlation. We discuss only 2^3P because $(\epsilon_{\text{psi}} - \tilde{\epsilon}_{\text{psi}})/\tilde{\epsilon}_{\text{psi}} = 0.23$ is much larger for 2^3P than 2^1P and indicates a greater possibility for change. Minimization of the expectation value of H with $\phi_{\text{RHF}} + \chi_{\text{psi}}$ [i.e., Eq. (40)], where the coefficients of the $5d$ -symmetry STO's in the "d" of Eq. (14) were varied, gave

$$\tilde{\epsilon}_{\text{psi}}(\text{separately minimized}) = -0.000048 \text{ a.u. } (-0.00131 \text{ eV}). \quad (43)$$

The separately determined $\tilde{\epsilon}_{\text{psi}}$ differs from the value extracted from GKJ by 4%, and, at least in this simple case, indicates the error to be expected when the polarization and semi-internal correlation is calculated separately from the pair correlation functions.

Although here it is shown that there is no significant

loss in accuracy to calculate semi-internal correlation and polarizations separately from the pair correlations to which they were directly related, it is probably *a fortiori* true that they can be calculated separately from pair correlations⁷ to which they are not related, as in larger atoms and molecules. Nevertheless, the $1s2p$ system might not be that representative of larger systems, so any generalizations from $1s2p$ He must be regarded as having some speculative character.

V. SUMMARY

The correlation energies of the 2^1P and 2^3P states of He have been analyzed into physically meaningful correlation effects. The $1s2p$ pair correlation accounts for approximately 90% of the total correlation energies, and the d -symmetry polarization of the $1s$ orbital plus $(1s, 2p_i; 2p_j)$ -type semi-internal correlation account for approximately half of the remaining variational energy. The modification of the $2p$ orbital, $\hat{f}_{2p}^{(\text{eco})}$, via interaction with \hat{u}_{1s2p} accounts for the remaining correlation energy. The polarization and semi-internal correlation effects can be accurately calculated independently from the pair correlation effects, but the $\hat{f}_{2p}^{(\text{eco})}$ cannot.

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