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Atomic Bethe-Goldstone Equations. IV. Valence-Shell Correlation Energies of Ground States of Na, Mg, Al, Si, P, S, Cl, and Ar

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Correlation energies for *M*-shell and mixed *LM*-shell electron pairs have been computed for the ground states of the atoms listed in the title. For open-shell atomic states, one-electron effective correlation energies are also computed. The method used is a formulation of Brueckner's theory in which one- and two-particle Bethe-Goldstone equations are solved by a variational procedure that uses *N*-particle trial wave functions expressed as linear combinations of Slater determinants. Individual pair-correlation energies are computed to an expected accuracy of a few percent, based on previous calculations on *L*-shell atoms. The computed correlation-energy data are used to analyze the various energy contributions to the first ionization potentials of the atoms considered.

I. INTRODUCTION

This paper extends calculations of electronic-correlation energies to atoms of the third chemical period, using a method applied previously to atoms of the second period.[1] The method used is an application of Brueckner's many-particle theory[2] to the electronic structure of atoms. For closed-shell states, as in the case of the ^1S ground states of Mg and Ar considered here, the only difference of the present work from the Brueckner theory is the use of a Hartree-Fock set of electronic orbitals, avoiding the higher level of self-consistency implied by Brueckner's original formulation. This use of Hartree-Fock rather than Brueckner self-consistency for electronic theory has been discussed some time ago.[3] The essential aspect of Brueckner's theory that is used is the independent solution of two-particle equations for each pair of occupied orbitals in an assumed Fermi sea. This procedure is characterized by Gomes *et al.*[4] as the "independent-pair model."

The two-particle equations of Brueckner's theory, embodying the independent-pair model, were first derived as differential equations by Bethe and Goldstone,[5] and are commonly known as Bethe-Goldstone equations. Several forms of these two-particle equations have been discussed in the extensive literature on Brueckner's theory. In the original formulation of Brueckner, the two-particle equation took the form of an integral equation.[2] The equivalent differential equation, with an orthogonality constraint, was derived by Bethe and Goldstone.[5] The Bethe-Goldstone equation was shown to be equivalent to a sum of so-called ladder diagrams in many-particle perturbation theory by Goldstone.[6] The two-particle variational equation proposed by Sinanoğlu[7] and referred to by him as an "exact-pair" equation is equivalent to the Bethe-Goldstone equation as given for atomic electrons by Szasz,[8] except for a possibly unimportant difference in treatment of the residual one-electron perturbing operator.[9]

In the present work, this formalism is recast as a many-particle method, involving a hierarchy of variational calculations equivalent to the usual Bethe-Goldstone equation at the two-particle level of the hierarchy.[10,11] The only aspect of this formalism used in the calculations to be reported here that represents any conceptual advance over the Brueckner theory is the treatment of one-electron energy effects in open-shell atomic states. This requires one-particle Bethe-Goldstone equations, defined in a consistent way as the one-particle level of the hierarchy of equations considered in the present work.

Previous calculations of electronic pair-correlation energies have been carried out on Be[12] and the $2s^2$ valence pair of several atoms,[13] using Sinanoğlu's method. The present method has been applied to correlation energies in ground states of atoms from Be through Ne[10] and to calculations of hyperfine-structure constants.[11] The calculations to be reported here extend this work to one- and two-electron correlation energies affecting the *M*-shell valence orbitals (3*s* and 3*p*) of the ground states of atoms from Na through Ar.

II. METHOD OF COMPUTATION

If a Fermi sea is defined for *N* electrons by the occupied orbitals of a reference-state Slater determinant Φ_0, the Bethe-Goldstone equation for pair *ij* is a two-particle Schrödinger equation, constrained by requiring the wave function to be orthogonal to the $N-2$ occupied orbitals ϕ_k of Φ_0 with $k \neq i$ or j.[8] This is equivalent to a variational calculation with an *N*-particle trial function[9,10]

$$\Psi_{ij} = \Phi_0 + \textstyle\sum_a \Phi_i^a c_i^a + \sum_b \Phi_j^b c_j^b + \sum_{ab} \Phi_{ij}^{ab} c_{ij}^{ab} . \quad (1)$$

TABLE I. Exponents used for orbital basis sets.

Z	Atom	ζ_L	ζ_M
11	Na	3.191	1.035
12	Mg	3.565	1.228
13	Al	3.939	1.421
14	Si	4.313	1.614
15	P	4.687	1.807
16	S	5.067	2.006
17	Cl	5.447	2.204
18	Ar	5.826	2.403

In the notation used here, a Slater determinant obtained from Φ_0 by replacing occupied orbitals ϕ_i, $\phi_j, \ldots$ $(i < j \ldots \leq N)$ by unoccupied orbitals ϕ_a, $\phi_b, \ldots (N < a < b \ldots)$, chosen from a postulated countable complete set of orbital functions, is denoted by $\Phi_{ij\cdots}^{ab\cdots}$. In Eq. (1), the summations extend over all values of the indices a and b, but indices i and j are fixed and denote specific occupied orbitals in Φ_0. The summation over ab denotes a double sum with $a < b$.

A first-order or one-particle Bethe-Goldstone equation is defined to be equivalent to a variational calculation with trial function

$$\Psi_i = \Phi_0 + \sum_a \Phi_i^a c_i^a , \qquad (2)$$

where index i is specified, but a takes on all possible values.

The coefficients such as c_i^a or c_{ij}^{ab} are obtained as components of an eigenvector of the matrix of the N-electron Hamiltonian H over the set of Slater determinants included in the variational trial function. This reduces the Bethe-Goldstone calculation to a straightforward configuration-interaction calculation. As indicated by Eq. (1) or (2), it is convenient to normalize the wave function by setting the coefficient of Φ_0 equal to unity. The reference state Φ_0 is a Hartree-Fock determinant computed with the usual symmetry and equivalence restrictions for open-shell atomic states.[14]

In practice, the set of unoccupied orbitals ϕ_a is finite. Orbital sets are used that can be extended to completeness, and this extension is carried out until computed quantities are observed to stabilize within a specified error. The pattern of basis truncation used here is expected to give errors no greater than 0.001 Hartree a.u. (e^2/a_X for atom X) in the largest pair-correlation energies.

The energy eigenvalue computed directly for trial function $\Psi_{ij\ldots}$ is the gross energy increment $\Delta E_{ij\ldots}$, an energy mean-value correction relative to the Hartree-Fock energy H_{00}. The *net* increment $e_{ij\ldots}$ is defined as the difference between $\Delta E_{ij\ldots}$ and the sum of all net increments of lower order, with indices that are a proper subset of the indices $ij\ldots$. For example, the net energy increment for pair 2, 5 is

$$e_{25} = \Delta E_{25} - e_2 - e_5 , \qquad (3)$$

where ΔE_{25} is the directly computed lowest eigenvalue of the configuration-interaction matrix for Ψ_{25}, and e_2 and e_5 are net increments obtained from first-order Bethe-Goldstone equations for Ψ_2 and Ψ_5, respectively. If carried to Nth order, this method of bookkeeping gives the exact correlation energy (energy in addition to H_{00})

$$\Delta E = \sum_i e_i + \sum_{ij} e_{ij} + \sum_{ijk} e_{ijk} + \cdots e_{1\ldots N} . \qquad (4)$$

Each net increment has been shown to be equivalent to a particular sum of Goldstone diagrams in the formal linked-cluster perturbation theory,[6] summed in each case to infinite order.[1] Thus, the decomposition of the correlation energy in the present method is essentially different from that implied by perturbation theory, although both methods eventually converge to the exact result.

The atoms considered here have single-determinant wave functions in their ground states, if M_L and M_S are taken equal to L and S, respectively. The constraints inherent in the traditional Hartree-Fock method introduce one-particle configuration-interaction matrix elements for states other than ^1S. These matrix elements, which cannot be eliminated without destroying the spherical-symmetry properties of the Hartree-Fock orbitals, lead to nonzero one-particle net-correlation-energy contributions. The configuration-interaction matrix is constructed in a basis of Slater determinants, taking into account only the quantum numbers M_L, M_S, and parity.

TABLE II. One-particle net increments of correlation energy e_i in Hartree units (e^2/a_χ) for atom χ.

i	Na(^2S)	Mg(^1S)	Al(^2P)	Si(^3P)	P(^4S)	S(^3P)	Cl(^2P)	Ar(^1S)
$3s\beta$		−0.0	−0.000382	−0.000457	−0.000177	−0.000692	−0.000649	−0.0
$3s\alpha$	−0.0	−0.0	−0.000516	−0.000593	−0.000141	−0.000455	−0.000422	−0.0
$3p_{-1}\beta$								−0.0
$3p_0\beta$							−0.000096	−0.0
$3p_1\beta$						−0.000631	−0.000096	−0.0
$3p_{-1}\alpha$					−0.0	−0.000150	−0.000215	−0.0
$3p_0\alpha$				−0.0	−0.0	−0.000387	−0.000193	−0.0
$3p_1\alpha$			−0.0	−0.0	−0.0	−0.000150	−0.000215	−0.0

TABLE III. Two-particle net increments of correlation energy e_{ij} for *LM* pairs (Hartree units).

ij	Na(^2S)	Mg(^1S)	Al(^2P)	Si(^3P)	P(^4S)	S(^3P)	Cl(^2P)	Ar(^1S)
$2s\beta\ 3s\beta$		−0.000 271	−0.000 371	−0.000 441	−0.000 494	−0.000 481	−0.000 447	−0.000 397
$2s\alpha$		−0.000 546	−0.000 762	−0.000 909	−0.001 013	−0.001 062	−0.001 074	−0.001 069
$2p_{-1}\beta$		−0.001 410	−0.001 707	−0.001 897	−0.001 985	−0.001 677	−0.001 341	−0.001 057
$2p_0\beta$		−0.001 419	−0.001 753	−0.001 873	−0.001 996	−0.001 839	−0.001 333	−0.001 061
$2p_1\beta$		−0.001 410	−0.001 707	−0.001 897	−0.001 985	−0.001 788	−0.001 561	−0.001 057
$2p_{-1}\alpha$		−0.001 737	−0.002 171	−0.002 440	−0.002 474	−0.001 991	−0.001 703	−0.001 588
$2p_0\alpha$		−0.001 750	−0.002 216	−0.002 330	−0.002 488	−0.002 278	−0.001 919	−0.001 593
$2p_1\alpha$		−0.001 737	−0.002 103	−0.002 352	−0.002 474	−0.002 379	−0.002 206	−0.001 588
$2s\beta\ 3s\alpha$	−0.000 360	−0.000 546	−0.000 715	−0.000 817	−0.000 871	−0.000 952	−0.001 019	−0.001 069
$2s\alpha$	−0.000 178	−0.000 271	−0.000 331	−0.000 346	−0.000 331	−0.000 365	−0.000 379	−0.000 397
$2p_{-1}\beta$	−0.001 321	−0.001 737	−0.001 756	−0.001 658	−0.001 604	−0.001 753	−0.001 699	−0.001 588
$2p_0\beta$	−0.001 333	−0.001 750	−0.001 929	−0.001 805	−0.001 610	−0.001 683	−0.001 580	−0.001 593
$2p_1\beta$	−0.001 321	−0.001 737	−0.002 027	−0.002 006	−0.001 604	−0.001 561	−0.001 596	−0.001 588
$2p_{-1}\alpha$	−0.001 113	−0.001 410	−0.001 378	−0.001 258	−0.001 031	−0.001 051	−0.001 067	−0.001 057
$2p_0\alpha$	−0.001 122	−0.001 419	−0.001 509	−0.001 238	−0.001 036	−0.001 074	−0.001 055	−0.001 061
$2p_1\alpha$	−0.001 113	−0.001 410	−0.001 479	−0.001 396	−0.001 031	−0.000 929	−0.001 067	−0.001 057
$2s\beta\ 3p_{-1}\beta$								−0.000 559
$2s\alpha$								−0.000 775
$2p_{-1}\beta$								−0.000 561
$2p_0\beta$								−0.001 212
$2p_1\beta$								−0.001 485
$2p_{-1}\alpha$								−0.001 607
$2p_0\alpha$								−0.001 413
$2p_1\alpha$								−0.002 015
$2s\beta\ 3p_0\beta$							−0.000 516	−0.000 559
$2s\alpha$							−0.000 728	−0.000 775
$2p_{-1}\beta$							−0.001 257	−0.001 209
$2p_0\beta$							−0.000 790	−0.000 843
$2p_1\beta$							−0.001 133	−0.001 209
$2p_{-1}\alpha$							−0.001 318	−0.001 411
$2p_0\alpha$							−0.002 067	−0.002 224
$2p_1\alpha$							−0.001 323	−0.001 411
$2s\beta\ 3p_1\beta$						−0.000 380	−0.000 535	−0.000 559
$2s\alpha$						−0.000 682	−0.000 760	−0.000 775
$2p_{-1}\beta$						−0.001 491	−0.001 560	−0.001 485
$2p_0\beta$						−0.001 264	−0.001 145	−0.001 212
$2p_1\beta$						−0.000 404	−0.000 548	−0.000 561
$2p_{-1}\alpha$						−0.001 696	−0.001 888	−0.002 015
$2p_0\alpha$						−0.001 213	−0.001 336	−0.001 413
$2p_1\alpha$						−0.001 385	−0.001 537	−0.001 607
$2s\beta\ 3p_{-1}\alpha$					−0.000 598	−0.000 546	−0.000 729	−0.000 775
$2s\alpha$					−0.000 402	−0.000 461	−0.000 517	−0.000 559
$2p_{-1}\beta$					−0.001 370	−0.001 602	−0.001 646	−0.001 607
$2p_0\beta$					−0.001 218	−0.001 467	−0.001 345	−0.001 413
$2p_1\beta$					−0.001 687	−0.001 645	−0.001 918	−0.002 015
$2p_{-1}\alpha$					−0.000 454	−0.000 489	−0.000 536	−0.000 561
$2p_0\alpha$					−0.000 985	−0.001 080	−0.001 155	−0.001 212
$2p_1\alpha$					−0.001 203	−0.001 315	−0.001 420	−0.001 485
$2s\beta\ 3p_0\alpha$				−0.000 498	−0.000 599	−0.000 683	−0.000 726	−0.000 775
$2s\alpha$				−0.000 329	−0.000 402	−0.000 382	−0.000 510	−0.000 559
$2p_{-1}\beta$				−0.001 035	−0.001 215	−0.001 444	−0.001 436	−0.001 411
$2p_0\beta$				−0.001 566	−0.001 856	−0.002 206	−0.002 084	−0.002 224
$2p_1\beta$				−0.001 037	−0.001 215	−0.001 260	−0.001 333	−0.001 411
$2p_{-1}\alpha$				−0.000 927	−0.000 982	−0.000 993	−0.001 144	−0.001 209
$2p_0\alpha$				−0.000 589	−0.000 681	−0.000 755	−0.000 792	−0.000 843
$2p_1\alpha$				−0.000 848	−0.000 982	−0.001 082	−0.001 144	−0.001 209

TABLE III. (*continued*)

ij	Na(^2S)	Mg(^1S)	Al(^2P)	Si(^3P)	P(^4S)	S(^3P)	Cl(^2P)	Ar(^1S)
$2s\beta\ 3p_1\alpha$			−0.000 372	−0.000 510	−0.000 598	−0.000 681	−0.000 745	−0.000 775
$2s\alpha$			−0.000 241	−0.000 336	−0.000 402	−0.000 345	−0.000 517	−0.000 559
$2p_{-1}\beta$			−0.001 092	−0.001 437	−0.001 687	−0.001 950	−0.002 035	−0.002 015
$2p_0\beta$			−0.000 801	−0.001 040	−0.001 218	−0.001 468	−0.001 346	−0.001 413
$2p_1\beta$			−0.000 893	−0.001 179	−0.001 370	−0.001 418	−0.001 537	−0.001 607
$2p_{-1}\alpha$			−0.000 877	−0.001 141	−0.001 203	−0.001 192	−0.001 420	−0.001 485
$2p_0\alpha$			−0.000 719	−0.000 851	−0.000 985	−0.001 074	−0.001 155	−0.001 212
$2p_1\alpha$			−0.000 319	−0.000 404	−0.000 454	−0.000 495	−0.000 536	−0.000 561

The lowest eigenvalue and eigenvector are obtained by a rapidly converging iterative algorithm.[15]

Orbital basis sets capable of giving a reasonable approximation to an atomic Hartree-Fock calculation, using the matrix Hartree-Fock method,[16] are extended by including additional orbitals in the form of exponential functions $e^{(-\zeta r)}$ multiplied by powers of r and by spherical harmonics. Optimal values of the exponent ζ were determined by preliminary calculations on Mg, Si, and Ar. Different values of ζ were used to represent perturbations of atomic orbitals with different principal quantum numbers n. Exponents ζ_L and ζ_M were obtained variationally for virtual excitations of the L and M shells, respectively, of Mg, Si, and Ar. Exponents for the other atoms considered here, listed in Table I, were obtained by linear interpolation. Virtual excitations of the K shell were not considered.

Orbital basis sets used in the present calculations have the same structure as those used previously for the atoms Be through Ne.[1] The basis sets contain orbitals capable of representing virtual orbitals with all combinations of up to three nodal surfaces superimposed on occupied Hartree-Fock orbitals. The specific basis sets used consist of the "double-ζ" basis set of Clementi[17] augmented by perturbing orbitals with exponents ζ_L and ζ_M as described above. All basis orbitals of s and p symmetry are included in a preliminary matrix Hartree-Fock calculation for each independent Bethe-Goldstone calculation. Gross energy increments are computed relative to this particular approximate Hartree-Fock energy in each case.

For calculations of energy increments e_i or e_{ij}, where i and j both denote M-shell orbitals, only perturbing orbitals with exponent ζ_M are included in the basis set. The basis for Mg is M-9532, denoting the double-ζ basis extended to nine s orbitals, five p orbitals, three d orbitals, and two f orbitals. For Al through Ar, the corresponding basis set is M-9632. Intershell energy increments e_{ij}, where i denotes an L-shell orbital and j denotes an M-shell orbital, are computed with basis sets LM-11 753 for Na and Mg; LM-11 953 for Al through Cl; and LM-12 953 for Ar.

III. RESULTS

The reference-state Slater determinants for the atomic ground states considered here, denoting filled inner shells $1s^2$ and $2s^2\,2p^6$ by K^2 and L^8, respectively, are

$$\begin{aligned}
&\Phi_0\ (\text{Na},\ {}^2S) = \det(K^2\,L^8\,3s\alpha),\\
&\Phi_0\ (\text{Mg},\ {}^1S) = \det(K^2\,L^8\,3s\beta\,3s\alpha),\\
&\Phi_0\ (\text{Al},\ {}^2P) = \det(K^2\,L^8\,3s\beta\,3s\alpha\,3p_1\alpha),\\
&\Phi_0\ (\text{Si},\ {}^3P) = \det(K^2\,L^8\,3s\beta\,3s\alpha\,3p_0\alpha\,3p_1\alpha), \quad (5)\\
&\Phi_0\ (\text{P},\ {}^4S) = \det(K^2\,L^8\,3s\beta\,3s\alpha\,3p_{-1}\alpha\,3p_0\alpha\,3p_1\alpha),\\
&\Phi_0\ (\text{S},\ {}^3P) = \det(K^2\,L^8\,3s\beta\,3s\alpha\,3p_1\beta\,3p_{-1}\alpha\,3p_0\alpha\\
&\qquad 3p_1\alpha),\\
&\Phi_0\ (\text{Cl},\ {}^2P) = \det(K^2\,L^8\,3s\beta\,3s\alpha\,3p_0\beta\,3p_1\beta\,3p_{-1}\alpha\\
&\qquad 3p_0\alpha\,3p_1\alpha),\\
&\Phi_0\ (\text{Ar},\ {}^1S) = \det(K^2\,L^8\,3s\beta\,3s\alpha\,3p_{-1}\beta\,3p_0\beta\,3p_1\beta\\
&\qquad 3p_{-1}\alpha\,3p_0\alpha\,3p_1\alpha).
\end{aligned}$$

One-particle net-correlation-energy increments, computed as described in Sec. II for the occupied $3s$ and $3p$ valence-shell orbitals, are listed in Table II. Two-particle net correlation energies for intershell LM pairs of orbitals, computed as in Eq. (3) from directly computed gross energy increments, are listed in Table III. Two-particle net correlation energies computed for intrashell M-orbital pairs are listed in Table IV. These data are summarized in Table V by listing for each atom the subtotals, respectively, of M-shell one-particle correlation-energy increments, of LM-shell pair-correlation energies, and of MM-shell pair-correlation energies (net energy increments).

Pair-correlation energies computed by the method used here depend in general on the quantum numbers m_l and m_s for each orbital of the pair. Except for ^1S states, the effective potential field of the open $3p$ shell is not spherically symmetrical, leading to m_l dependence. However, as found previously for lighter atoms,[1] the various $3p^2$ energies can be represented as linear combinations of only three parameters, using coefficients given previously,[10] to

TABLE IV. Two-particle net increments of correlation energy e_{ij} for *MM* pairs (Hartree units).

ij		Mg(^1S)	Al(^2P)	Si(^3P)	P(^4S)	S(^3P)	Cl(^2P)	Ar(^1S)
$3s\beta$	$3s\alpha$	−0.033 751	−0.030 004	−0.022 696	−0.012 952	−0.012 230	−0.011 260	−0.010 263
	$3p_{-1}\beta$							−0.001 947
	$3p_0\beta$						−0.003 670	−0.001 954
	$3p_1\beta$					−0.007 126	−0.005 393	−0.001 947
	$3p_{-1}\alpha$				−0.023 742	−0.014 964	−0.009 661	−0.007 795
	$3p_0\alpha$			−0.022 795	−0.024 383	−0.019 610	−0.013 380	−0.007 853
	$3p_1\alpha$		−0.021 493	−0.024 028	−0.023 742	−0.022 588	−0.017 694	−0.007 795
$3s\alpha$	$3p_{-1}\beta$							−0.007 795
	$3p_0\beta$						−0.008 554	−0.007 853
	$3p_1\beta$					−0.010 025	−0.009 853	−0.007 795
	$3p_{-1}\alpha$				−0.001 923	−0.001 995	−0.001 935	−0.001 947
	$3p_0\alpha$			−0.003 437	−0.001 931	−0.001 917	−0.002 039	−0.001 954
	$3p_1\alpha$		−0.006 276	−0.004 859	−0.001 923	−0.001 995	−0.001 935	−0.001 947
$3p_{-1}\beta$	$3p_0\beta$							−0.010 093
	$3p_1\beta$							−0.010 120
	$3p_{-1}\alpha$							−0.013 386
	$3p_0\alpha$							−0.011 890
	$3p_1\alpha$							−0.022 366
$3p_0\beta$	$3p_1\beta$						−0.009 817	−0.010 093
	$3p_{-1}\alpha$						−0.011 783	−0.011 890
	$3p_0\alpha$						−0.024 071	−0.024 477
	$3p_1\alpha$						−0.011 908	−0.011 890
$3p_1\beta$	$3p_{-1}\alpha$					−0.021 396	−0.022 206	−0.022 366
	$3p_0\alpha$					−0.012 205	−0.012 308	−0.011 890
	$3p_1\alpha$					−0.014 589	−0.014 610	−0.013 386
$3p_{-1}\alpha$	$3p_0\alpha$				−0.009 064	−0.009 439	−0.009 783	−0.010 093
	$3p_1\alpha$				−0.009 094	−0.009 479	−0.009 816	−0.010 120
$3p_0\alpha$	$3p_1\alpha$			−0.008 658	−0.009 064	−0.009 439	−0.009 783	−0.010 093

within the accuracy of the calculations. The values of these parameters are listed in Table VI.

IV. DISCUSSION

The purpose of the calculations reported here is to provide data for use in semiempirical estimates of net-correlation-energy contributions to differential energy changes in atoms and molecules. Such changes occur in electronic excitation, ionization or electron capture, and molecular dissociation. Such studies of net changes of correlation energy in the dissociation of diatomic molecules have demonstrated the need for quantitative data on pair-correlation energies.[18,19] Reliable data on total correlation energies are not directly available for atoms heavier than Ne, because the whole series of successive ionization potentials is not known accurately. Because calculations similar to those reported here on atoms from Be to Ne[1] resulted in total energies varying from 98.5 to 100.3% of the estimated empirical total correlation energies, the present results are expected to have similar accuracy. Thus, the data given here should be reliable to within a few percentage points.

Recent calculations on the ^1S ground state of Ne indicate that the convergence limit of the presence method, for a complete orbital basis set, would be approximately 106% of the empirical correlation energy.[20] This indicates that there is a cancellation of errors in the calculations. The error due to neglect of three- and four-particle net correlation energies is compensated by the error due to use of incomplete basis sets in the variational calculations.

TABLE V. Summary of one- and two-particle correlation energies (Hartree units).

	Na(^2S)	Mg(^1S)	Al(^2P)	Si(^3P)	P(^4S)	S(^3P)	Cl(^2P)	Ar(^1S)
$\sum e_i(M)$	−0.0	−0.0	−0.000 898	−0.001 050	−0.000 318	−0.002 465	−0.001 886	−0.0
$\sum e_{ij}(LM)$	−0.007 861	−0.020 560	−0.029 228	−0.038 390	−0.047 793	−0.057 411	−0.067 213	−0.076 610
$\sum e_{ij}(MM)$		−0.033 751	−0.057 773	−0.086 473	−0.117 818	−0.168 997	−0.221 459	−0.272 998

TABLE VI. Parameters for $3p^2$ pair-correlation energies (Hartree units).

	$\mathrm{Si}(^3P)$	$\mathrm{P}(^4S)$	$\mathrm{S}(^3P)$	$\mathrm{Cl}(^2P)$	$\mathrm{Ar}(^1S)$
$3p^2(^3P)$	− 0. 008 658	− 0. 009 074	− 0. 009 452	− 0. 009 800	− 0. 010 102
$3p^2(^1D)$			− 0. 014 589	− 0. 014 610	− 0. 013 386
$3p^2(^1S)$			− 0. 042 716	− 0. 042 993	− 0. 046 659

However, the results on L-shell atoms indicate that this cancellation occurs systematically and justifies the estimate given above of expected error in the present results.

As an illustration of the use of the data computed here, the electronic correlation energy contribution to the first ionization potentials of the atoms Na through Ar can be estimated. Neglecting KM intershell correlation, the sum of one- and two-particle net correlation energies $\epsilon_i + \sum_j \epsilon_{ij}$ for the valence orbital ϕ_i is obtained from Tables II, III, and IV and listed in Table VII. In Table VIII, these data are combined with the Hartree-Fock energy differences (rearrangement energy) to estimate the ionization potentials. The discrepancy with respect to spectroscopic values of the ionization potentials is considerably larger than the expected error in the computed correlation-energy contributions.

The only relativistic effect expected to be significant for valence-shell ionization potentials is the spin-orbit splitting. The observed ionization potential is the energy difference between the lowest J level of the ground-state L-S term of the positive ion and the lowest level of the neutral atom. The computed ionization potential, which neglects spin-orbit coupling, is the energy difference between the weighted average of J levels in each L-S term. The correction ΔE_{so}, to be added to the calculated ionization potential, has been computed by averaging the relative excitation energy of the observed J levels. This correction is given in Table VIII, and is obviously too small to account for the difference between computed and observed ionization potentials.

The remaining relativistic contribution to these ionization potentials is indicated by the calculations of Clementi[21] to be less than 0. 001 Hartree units (0. 03 eV) for the ground states of the atoms considered here. However, a complete quantitative treatment of relativistic and electrodynamic effects (Lamb shift) has not yet been carried out for many-electron atoms, and all published numbers must be considered somewhat tentative.

The effect of three-and four-particle correlation has not been taken into account in the present calculations. Results for lighter atoms indicate that these higher-order correlation terms tend to reduce the magnitude of the correlation energy computed from one-and two-particle terms only.[10] In particular, recent calculations on $\mathrm{Ne}(^1S)$ indicate that the sum of two-electron net correlation energies is 6% larger than the empirical total,[20] so this amount of reduction must be attributed to three-and four-particle terms. The dominant effects are due to coupling of virtual excitations of valence-shell orbitals.

The discrepancy, shown in Table VIII, between computed and observed ionization potentials increases as the valence M shell fills, and requires a reduction of the magnitude of the correlation energy ΔE_{corr} to bring the computed values into agreement with experiment. This is exactly the behavior expected of three-and four-particle correlation effects in the valence shell, and suggests that this is the principal cause of the discrepancy. This point will be considered in more detail in a later publication.

V. REMARKS

The present work is based on Brueckner's many-particle theory,[2] but with modifications appropriate to the study of the electronic structure of atoms. In particular, the orbitals of the reference state are determined by Hartree-Fock equations, avoiding the time-consuming higher level of self-consistency implied by the original statement of Brueckner's theory.[2] This is justified for atomic electrons because of the general validity of the Hartree-Fock approxi-

TABLE VII. Correlation contribution to ionization energy of orbital i (Hartree units).

i	$\mathrm{Na}(^2S)$	$\mathrm{Mg}(^1S)$	$\mathrm{Al}(^2P)$	$\mathrm{Si}(^3P)$	$\mathrm{P}(^4S)$	$\mathrm{S}(^3P)$	$\mathrm{Cl}(^2P)$	$\mathrm{Ar}(^1S)$
$3s\beta$		− 0. 044 031	− 0. 064 669	− 0. 084 115	− 0. 099 905	− 0. 090 705	− 0. 073 291	− 0. 048 964
$3s\alpha$	− 0. 007 861	− 0. 044 031	− 0. 047 920	− 0. 042 109	− 0. 027 988	− 0. 037 985	− 0. 045 460	− 0. 048 964
$3p_{-1}\beta$								− 0. 087 224
$3p_0\beta$							− 0. 079 031	− 0. 087 891
$3p_1\beta$						− 0. 074 487	− 0. 083 592	− 0. 087 224
$3p_{-1}\alpha$					− 0. 051 740	− 0. 066 028	− 0. 074 665	− 0. 087 224
$3p_0\alpha$				− 0. 041 719	− 0. 052 374	− 0. 061 802	− 0. 080 726	− 0. 087 891
$3p_1\alpha$			− 0. 033 083	− 0.044 443	− 0. 051 740	− 0. 066 863	− 0. 075 252	− 0. 087 224

TABLE VIII. Analysis of first ionization potential (IP) (Hartree units unless otherwise indicated).

Atom	Na(^2S)	Mg(^1S)	Al(^2P)	Si(^3P)	P(^4S)	S(^3P)	Cl(^2P)	Ar(^1S)
Orbital	$3s\alpha$	$3s\beta$	$3p_1\alpha$	$3p_0\alpha$	$3p_{-1}\alpha$	$3p_1\beta$	$3p_0\beta$	$3p_{-1}\beta$
$E_{\mathrm{SCF}}(N)$ [a]	−161.85857	−199.61432	−241.87630	−288.85420	−340.71857	−397.50469	−459.48179	−526.81705
$E_{\mathrm{SCF}}(N-1)$ [a]	−161.67676	−199.37132	−241.67408	−288.57276	−340.34947	−397.17285	−459.04839	−526.27429
ΔE_{SCF}	0.18181	0.24300	0.20222	0.28144	0.36910	0.33184	0.43340	0.54276
ΔE_{corr} [b]	0.00786	0.04403	0.03308	0.04172	0.05174	0.07449	0.07903	0.08722
IP	0.18967	0.28703	0.23530	0.32316	0.42084	0.40633	0.51243	0.62998
IP (eV)	5.161	7.810	6.403	8.794	11.451	11.057	13.944	17.142
$\mathrm{IP}_{\mathrm{obs}}$ (eV) [c]	5.138	7.644	5.984	8.149	11.0	10.357	13.01	15.755
ΔE_{so} (eV) [d]	0.0	0.0	0.009	−0.005	−0.039	0.024	−0.006	−0.059

[a] E. Clementi, *Tables of Atomic Functions* (IBM Corporation, San Jose, Calif., 1965).

[b] Data from Table VII.

[c] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S. GPO, Washington, D. C. 1949), Vol. I.

[d] Spin-orbit contribution to the observed ionization potential.

mation.[3] The other, and more important, aspect of Brueckner's theory, the independent-pair model,[4] is used here explicitly in the form of variational equations equivalent to the two-particle Bethe-Goldstone equation given for atomic electrons by Szasz.[8]

It has been shown[10] that Brueckner's theory, as used here, can be put into the context of an ultimately convergent computational procedure based on the definition of Bethe-Goldstone equations for clusters of n particles of an N-particle system, where $n = 1, 2, \ldots N$. Correlation energy and mean values of physical operators are computed by succesive calculations of terms of increasing order in this hierarchy of Bethe-Goldstone equations.[10] The principal corrections to two-particle net correlation energies, as computed here, are expected in this procedure to come from three- and four-particle net correlation energies, computed from the appropriate variational equations.[10] Calculations of such three- and four-particle energy terms, carried out in special cases,[10] indicate that they are individually small compared with two-particle terms, although there is always the possibility that a large number of small terms could add up to a significant correction.

The present calculations use orbital basis sets of exactly the same form as earlier systematic calculations on the ground states of atoms from Be to Ne.[1] These calculations gave total correlation energies, evaluated as the sum of two-particle net correlation energies, varying within 1 or 2% of the empirically known total correlation energies. It would be surprising if the present results were significantly less accurate, but no direct test is possible because the empirical correlation energies are not known for the atoms considered here.

In the case of Ne (^1S), it has been possible to carry out a calculation[20] with an orbital basis set very much larger than those used for the series of atoms considered previously.[1] This calculation, with orbitals up to $l = 6$, is a *tour de force* that could not be repeated for the whole series of atoms up to Ar. The resulting sum of pair-correlation energies indicates that the limit of completeness is roughly 6% greater than the empirical correlation energy, and 8% greater than the original calculation with a smaller orbital basis set. In the hierarchical formalism used here, this excess must be compensated by higher-order net energy terms, presumably by the three- and four-particle terms. Hence, the originally computed value, 98% of the empirical correlation energy for Ne (^1S), involves a fortuitous cancellation between the truncation error (orbital incompleteness) and the compensating effect of three- and four-particle terms. Because the present calculations on heavier atoms are identical in structure (choice of basis sets) to the earlier work, the same kind of fortuitous cancellation is expected in the present results.

It should be emphasized that the *exact* (nonrelativistic) many-electron Hamiltonian is used in evaluating matrix elements used in the variational calculations of the present work. Details of the method have been given in earlier publications.[10] Two-electron corrections are automatically taken into account in the formulas for diagonal energies of virtual excited states. This contrasts with the case of perturbation theory, where these two-electron effects appear as explicit corrections to one-electron Hartree-Fock energies.

Thus, no special provision has to be made for these effects in the present formalism.

Further work is needed to resolve the discrepancy indicated here in the attempt to estimate the effect of electronic correlation on ground-state ionization potentials. Because the correlation correction is found to be too large, the discrepancy will be increased by use of a more complete orbital basis set, which will increase the magnitude of computed pair-correlation energies. The effect of three-particle terms is the most likely source of the discrepancy, which increases markedly with the number of valence electrons, as would the total effect of three-particle terms. However, it is also necessary to do comparable two-electron calculations on the positive ions rather than assuming, as is done here, that the individual pair-correlation terms are the same for atom and ion. There is an expected differential effect on the ionization potential, of the right sign to diminish the present discrepancy, due to the contraction of the valence orbitals in the ion with respect to those of the neutral atom. This will increase the magnitude of pair-correlation terms in the ion, and reduce the net contribution of electronic correlation to the ionization potential. Systematic calculations on the positive ions, and calculations of three-particle net-correlation-energy terms are needed.

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