Atomic Bethe-Goldstone Equations. II. The Ne Atom

R. K. Nesbet

IBM Research Laboratory, San Jose, California

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The nonrelativistic electronic energy of Ne(^1S) is computed by the variational solution of generalized Bethe-Goldstone (BG) equations. The sum of all two-particle net energy increments (pair correlation energies) is -0.3822 atomic units (a.u.), or 97.3% of the empirical correlation energy. The three- and four-particle net energy terms expected to be most important are computed and found to be smaller than 0.001 a.u. The computed pair correlation energies are analyzed in terms of symmetries induced in the BG equations, and are found to be represented well within the accuracy of the present calculations by the somewhat smaller number of parameters needed to characterize the L and S eigenstates of all possible eight-particle subsystems of the ten-electron Hartree-Fock reference state.

I. INTRODUCTION

THIS paper reports the results of a calculation of the nonrelativistic electronic correlation energy of the neon atom in its ^1S ground state. The method used, variational solution of Bethe-Goldstone (BG) equations, has been applied previously to calculations of the correlation energy[1] of Be and of the energy and hyperfine structure constant of Li(^2S) and N(^4S).[2,3]

The method of superposition of configurations was used by Bernal and Boys[4] and by Donath[5] to compute, respectively, -0.1514 and -0.2008 atomic units (a.u.) [2Ry(Ne)] for the correlation energy of Ne(^1S). These results are to be compared with Clementi's empirical value of the Ne correlation energy, -0.393 a.u.[6] Both of these calculations attempted to solve the Schrödinger equation directly as a 10-particle problem.

In the present work, a similar variational method (superposition of configurations) is applied in turn to a sequence of *nth-order* BG equations. This terminology describes the time-independent Schrödinger equation for n particles embedded in the Fermi sea of $N-n$ particles, the remainder of an N-particle system. The Fermi sea is taken to be that described by the N occupied orbitals of the ground-state Hartree-Fock (HF) wave function. This definition of higher-order BG equations makes it possible to compute the net increments of energy (or of any physical quantity expressed as an expectation value) in successively higher orders, terminating the calculations when the net increments are found to be negligible. The net increments themselves become well-defined quantities that can be computed by a variety of methods, making it possible to reach a definitive answer to questions regarding their importance in any particular context.

The second-order BG equations,[7] based on the work of Brueckner,[8] have been thoroughly discussed in the context of nuclear theory. The "exact pair" equations of Sinanoğlu,[9] essentially the same as the second-order BG equations,[10] have been used recently for atomic-wave-function calculations. Despite some slight differences in the formalism, the $2s^2$ pair correlation energy computed by McKoy and Sinanoğlu[11] for Ne should be identified with the second-order net correlation energy increment $e(2s\beta,2s\alpha)$ computed here. In the present work, all independent second-order terms are computed, as well as some of the higher-order terms expected to be most important.

II. OUTLINE OF COMPUTATIONAL METHOD

A preliminary matrix HF calculation[12] is carried out. This determines an orthonormal set of orbital functions, each expressed as the product of a radial function and a spherical harmonic and spin eigenfunction. The radial factors are linear combinations of a set of basis functions of the form

$$r^{n-1}\exp(-\zeta r),\qquad(1)$$

multiplied by a normalizing factor. The HF calculation divides the orthonormal set of orbitals into two sets: N orbitals ϕ_i occupied in a single determinant ^1S wave function,

$$\Phi_0=\det\phi_1(1)\cdots\phi_n(N),\qquad(2)$$

and the remaining orbitals ϕ_a, unoccupied in the reference state Φ_0. Members of the orthonormal set of Slater determinants constructed by replacing occupied orbitals $ijk\cdots$ of Φ_0 by unoccupied orbitals $abc\cdots$ will be denoted by $\Phi_{ijk\cdots}{}^{abc\cdots}$. For a given set of basis orbitals, a BG equation of order n is solved approximately by minimizing the energy mean value of a trial function

$$\Psi_{ijk\cdots}=\Phi_0+\sum_a\Phi_i{}^ac_i{}^a+\cdots+\sum_{ab}\Phi_{ij}{}^{ab}c_{ij}{}^{ab}+\cdots,\qquad(3)$$

[1] R. K. Nesbet, preceding paper, Phys. Rev. **155**, 51 (1967).

[2] R. K. Nesbet, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P.-O. Löwdin (Academic Press Inc., New York, 1966), pp. 157–165.

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[8] K. A. Brueckner, Phys. Rev. **96**, 508 (1954); **97**, 1353 (1955).

[9] O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962); **36**, 3198 (1962); Advan. Chem. Phys. **6**, 315 (1964).

[10] R. K. Nesbet, Advan. Chem. Phys. **9**, 321 (1965).

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

[12] R. K. Nesbet, Rev. Mod. Phys. **35**, 552 (1963).

where the only occupied orbital indices $ijk\cdots$ that occur as subscripts are those in a specified set of n indices.

The net increment of energy, or of any other physical expectation value, is obtained by subtracting from the computed gross increment,

$$(\Psi_{ijk}\ldots,F\Psi_{ijk}\ldots)(\Psi_{ijk}\ldots,\Psi_{ijk}\ldots)^{-1} - (\Phi_0, F\Phi_0), \quad (4)$$

the sum of all net increments of lower order with indices in the set $ijk\cdots$. This definition implies that the sum of all net increments up to order N is the exact expectation value, to the accuracy allowed by an initial choice of basis orbitals.

After considerable exploration of other possibilities, it was found that a relatively simple choice of basis orbital parameters gives results for pair correlation energies apparently accurate to 0.001 a.u., the criterion used in this work. The "double-zeta" basis set used by Clementi[13] for approximate HF calculations is augmented by two series of orbitals with angular quantum number l up to 3 and n up to 5. Each series has a single exponent, $\zeta_K = 21.63$ for K-shell excitations and $\zeta_L = 4.214$ for L-shell excitations. These exponents were determined by a series of preliminary calculations.

Specific basis sets used for the results reported here will be denoted by symbols such as K-8632 or L-6421. Here K-8632 denotes a basis set with double-zeta exponents 8.9141, 12.3545 for $1s$; 2.1839, 3.4921 for $2s$; 2.0514, 4.6748 for $2p$; and augmented by exponent 21.63 for $2s$, $3s$, $4s$, $5s$; $2p$, $3p$, $4p$, $5p$; $3d$, $4d$, $5d$; $4f$, $5f$. KL-8642 denotes the double-zeta set augmented by exponents 21.63 for $2s$, $3s$; 4.214 for $3s$, $4s$; 21.63 for $2p$, $3p$; 4.214 for $3p$, $4p$; 4.214 and 21.63 for $3d$, $4d$; 4.214 and 21.63 for $4f$. The basis set L-6421 is double-zeta plus exponent 4.214 for $3s$, $4s$; $3p$, $4p$; $3d$, $4d$; $4f$.

III. SECOND-ORDER BETHE-GOLDSTONE EQUATIONS

The first-order net energy increments are negligible, because of the use of a preliminary matrix HF calculation. The second-order net increments, or pair correlation energies, are listed in Table I. The $1s^2$ term was computed with basis set K-8642, described in Sec. II. The K,L terms were computed with basis set KL-8642, and the L,L terms with L-6421.

The only comparable result published previously is the $2s^2$ pair correlation energy computed by McKoy and Sinanoğlu[11] to be -0.272 eV or -0.0100 a.u., using a variational trial function that included relative coordinates. The present result for $e(2s\beta,2s\alpha)$ is -0.0108 a.u. The very substantial reduction of this quantity from its value in Be, -0.0454 a.u.,[1] can be attributed to the fact that the nearly degenerate $2p$ orbitals that interact strongly with $2s^2$ in Be are no longer available as unoccupied orbitals in Ne.[11,14]

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[14] R. K. Nesbet, J. Chem. Phys. **40**, 3619 (1964).

TABLE I. Pair correlation energies e_{ij} in Ne(^1S). Units are Hartree atomic units, a.u.(Ne), such that the electron reduced mass in Ne is unity. To convert to cm^{-1}, multiply by 0.2194686×10^6.

i,j	Weight	e_{ij}
$1s\beta,1s\alpha$	1	-0.039932
$1s\beta,2s\beta$	2	-0.000469
$1s\beta,2s\alpha$	2	-0.002099
$1s\beta,2p_0\beta$	6	-0.001481
$1s\beta,2p_0\alpha$	6	-0.001834
K, L subtotal		-0.025026
$2s\beta,2s\alpha$	1	-0.010834
$2s\beta,2p_{-1}\beta$	4	-0.003294
$2s\beta,2p_0\beta$	2	-0.003302
$2s\beta,2p_{-1}\alpha$	4	-0.010283
$2s\beta,2p_0\alpha$	2	-0.010317
$2p_{-1}\beta,2p_0\beta$	4	-0.010906
$2p_{-1}\beta,2p_1\beta$	2	-0.010927
$2p_{-1}\beta,2p_{-1}\alpha$	2	-0.016498
$2p_{-1}\beta,2p_0\alpha$	4	-0.013732
$2p_{-1}\beta,2p_1\alpha$	2	-0.022837
$2p_0\beta,2p_0\alpha$	1	-0.025813
L, L subtotal		-0.317269
$\sum e_{ij}$, all pairs		-0.382227

The calculations by Donath[5] included only configurations representing L-shell excitations. His computed correlation energy, -0.2008 a.u., can be compared with the total L-shell correlation energy given in Table I, -0.3173 a.u. This improvement is due to the very substantial increase in the number of excited configurations included in the present work.

The net energy increments e_{ij} listed in Table I are all computed independently. The programs used take account only of quantum numbers M_L, M_S, and parity, and the only obvious symmetry in the general BG equation is separate sign reversal of all quantum numbers m_l or m_s. The symmetry leads to the weights indicated in Table I for individual net energy increments. The near identity of some of these numbers arises from the underlying spherical symmetry of the Hamiltonian. Since the reference state Slater determinant Φ_0 is pure ^1S, if the $N-n$ particle Fermi sea is an eigenstate of $\mathbf{L}^2$ and $\mathbf{S}^2$, with quantum numbers L and S, the corresponding BG equation leads to an n-particle wave function with the same quantum numbers. This is a consequence of the fact that if two subsystems couple to an invariant state, they must have the same quantum numbers. For example, in the present calculations, the variational function $\Psi(1s\beta,1s\alpha)$ is a pure ^1S state to the full accuracy of the matrix diagonalization program, because the $N-n$ particle Fermi sea, $2s^2 2p^6$ in this case, is a ^1S closed shell configuration.

In the more general case, the $N-n$ particle Fermi sea will be a composite of states with several different values of (L,S). Because of the ^1S coupling of the complete wave function, the n-particle BG equation will be a composite of these same (L,S) values. For example, since the configuration $1s^2 2s^2 2p^4$ has three substates, ^3P, ^1D,

TABLE II. Parametrization of $2p^2$ pair correlation energies e_{ij}. The values of $e(^3P)$, $e(^1D)$, and $e(^1S)$ are listed in Table III.

	Coefficient of			
i,j	$e(^3P)$	$e(^1D)$	$e(^1S)$	e_{ij}, a.u. (Ne)
$2p_{-1}\beta,2p_0\beta$	1	0	0	-0.010913
$2p_{-1}\beta,2p_1\beta$	1	0	0	-0.010913
$2p_{-1}\beta,2p_{-1}\alpha$	0	1	0	-0.016498
$2p_{-1}\beta,2p_0\alpha$	$\frac{1}{2}$	$\frac{1}{2}$	0	-0.013706
$2p_{-1}\beta,2p_1\alpha$	$\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{3}$	-0.022898
$2p_0\beta,2p_0\alpha$	0	$\frac{2}{3}$	$\frac{1}{3}$	-0.025691

and ^1S, only three independent energy parameters should be needed to describe the six $2p^2$ pair correlation energies listed in Table I. The weights with which these occur in any p^4 state are well known, from analysis of the equivalent configurations p^4 or p^2, and lead to the coefficients listed in Table II. The parametrized values of e_{ij}, in the last column of Table II, agree with the directly computed values shown in Table I to well within the expected accuracy of the present calculations.

The full list of parameters needed to determine all of the pair correlation energies e_{ij} in Ne is given in Table III. Except for the $2p^2$ parameters, only the $1s2p$ and $2s2p$ parameters are not uniquely determined by the data in Table I. In these cases, a weighted average of the computed energies was used to determine the parameters. Because of the close agreement between computed values of $e(2s\beta,2p_{-1}\beta)$ and $e(2s\beta,2p_0\beta)$, which should both be equal and have the value -0.003297 a.u., and of $e(2s\beta,2p_{-1}\alpha)$ and $e(2s\beta,2p_0\alpha)$,both of which should equal -0.010295 a.u., when expressed in terms of the ^3P and ^1P $2s2p$ parameters, separate computation of $e(1s\beta,2p_{-1}\beta)$ and $e(1s\beta,2p_{-1}\alpha)$ was not carried out. It was considered justified to set these quantities equal to $e(1s\beta,2p_0\beta)$ and $e(1s\beta,2p_0\alpha)$, respectively, as indicated in Table I.

TABLE III. Pair correlation parameters for Ne(^1S), in Hartree atomic units, a.u.(Ne).

Pair	Value	Pair	Value
$1s^2(^1S)$	-0.039932	$2s2p(^3P)$	-0.003297
$1s2s(^3S)$	-0.000469	$2s2p(^1P)$	-0.017292
$1s2s(^1S)$	-0.003729	$2p^2(^3P)$	-0.010913
$1s2p(^3P)$	-0.001481	$2p^2(^1D)$	-0.016498
$1s2p(^1P)$	-0.002187	$2p^2(^1S)$	-0.044076
$2s^2(^1S)$	-0.010834		

IV. THIRD- AND FOURTH-ORDER EQUATIONS

In calculations[1] on Be it was found that the sum of all third-order net correlation energy increments e_{ijk} was somewhat less than 0.001 a.u. Because of the number of these terms for Ne, it was not feasible to compute all of them. Since these terms represent interference between the various second-order BG equations, it was anticipated that an especially large effect might arise from the mixing of excitations of orbitals $2s\beta$, $2p_0\beta$, and $2p_0\alpha$. The pair term involving the last two of these is the largest one computed for L-shell orbitals. With the basis set L-64 (s and p orbitals only), the net energy increment $e(2s\beta,2p_0\beta,2p_0\alpha)$ was computed to be 0.000261 a.u. If this is the largest such term, it appears to be justified to omit the third-order terms in work of the present accuracy.

As a further check of this conclusion, the fourth-order energy increment $e(2s\beta,2s\alpha,2p_0\beta,2p_0\alpha)$ was computed with the same basis set, but with the additional constraint of omitting the highest energy s and p orbital from the unoccupied HF set. The computed value is 0.000455 a.u. Since the sign is positive, the magnitude of this quantity could be reduced by an improved calculation.

V. DISCUSSION

The sum of all 45 two-particle net energy increments, given in Table I, is -0.382227 a.u. This is 97.3% of the empirical correlation energy, -0.393 a.u., estimated by Clementi.[6] Since the whole sequence of successive ionization potentials is not known experimentally, this figure is based on extrapolations of relativistic and nonrelativistic ionization potentials by Scherr et al.[15] The computed HF energy is then subtracted from the extrapolated total nonrelativistic energy. It is interesting to note that the difference between the present computed correlation energy and Clementi's estimate is of the same order of magnitude as the Lamb shift (radiative) correction, estimated to be 0.0086 a.u.[16] However, the present calculations are not quite accurate enough to give any information about the radiative correction, since each of the 45 pair correlation terms could have a residual error up to 0.001 a.u. The sum of three-particle terms is also indicated to be of this order of magnitude.

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[16] H. Hartmann and E. Clementi, Phys. Rev. 133, A1295 (1964).