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[10] The author is indebted to Professor J. R. Dorfman for pointing out an error in this expression as it appeared in an earlier manuscript.

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Nonsymmetric Perturbation Calculations of Excited States of Helium†

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Perturbation-theoretic calculations are carried out for the lowest five states of the helium atom using a Hamiltonian which is not symmetric in the particle indices such that the zeroth-order spatial functions can be written as simple products of hydrogenic orbitals. The perturbation expansions are reasonably convergent except for the fifth state which is divergent as expected. By 19th order in the expansion the energies of the first two excited states are accurate to 2×10^{-4} and the expectation values of $\frac{1}{2}(1\pm P)$ are accurate to 1×10^{-4}.

I. INTRODUCTION

It is general practice to perform perturbation-theoretic calculations using spatial functions Φ_0 which possess the exact many-electron symmetry. Thus, for example, the energies of the first two excited states of helium have been calculated with

$$\Phi_0^{1,3} = 1s(1)\,2s(2) \pm 2s(1)\,1s(2)\,, \tag{1}$$

as the unnormalized singlet and triplet zeroth-order functions constructed from hydrogenic 1s and 2s functions.[1,2] The splitting between the two energies is called the exchange energy since in lowest (first) order it is given by

$$J_1 = 2\,\langle 1s(1)\,2s(2)\,|\,r_{12}^{-1}\,|\,2s(1)\,1s(2)\rangle\,, \tag{2}$$

although, in fact, J_1 is larger than the exact J itself by a factor of 3.

There are, however, some advantages to choosing the functions Φ_0 to be simple products of atomic orbitals as was first discussed by Heisenberg[3] and later by Hartree,[4] but further attempts have been discouraged by the generally accepted view[5,6] that a systematic treatment of perturbation theory is impossible unless the exact permutation symmetry is incorporated into Φ_0 itself. The contrary view was expressed by Musher[7,8] in a discussion of the hydrogen molecule where the rather obvious point was made that if perturbation theory converges then the particle symmetry will be introduced order by order by the action of the nonsymmetric perturbation. A necessary requirement for such a procedure to be valid is that the spatial Φ_0 for a given state be a nondegenerate eigenfunction of its H_0 although this is by no means sufficient to assure convergence as will be appreciated from the discussion below. An analysis of the problem for many-electron systems has been given by Musher and Silbey[9] and Musher[10] and calculations have been performed by Schulman *et al.*[11] on the Li atom using this approach with a Hartree product Φ_0 giving reasonably accurate results by third order in electron correlation. A nonsymmetric Φ_0 for the hydrogen molecule, which avoids the symmetrization of the Heitler-London[12] valence-bond function, has been used by Saika and co-workers[13-15] to obtain reasonably good convergence for electromagnetic properties by first order in electron correlation. The present calculation on the excited states of the He atom provides the first convincing demonstration of the convergence of expansions based on nonsymmetric functions Φ_0 by utilizing the technique of Dalgarno and co-workers.[16,17] to evaluate the perturbation theory energies to high order.

II. PROCEDURE

We consider a zeroth-order Hamiltonian which is not symmetric under permutation of the particle indices, i.e.,

$$[H_0, P] \neq 0$$

as

$$H_0 = h_a(1) + h_b(2) \,, \tag{3}$$

where

$$h_a(1) = -\tfrac{1}{2}\nabla_1{}^2 - Z_a/r_1 \tag{4a}$$

and

$$h_b(2) = -\tfrac{1}{2}\nabla_2{}^2 - Z_b/r_2\, r \tag{4b}$$

The eigenfunctions of $h_a(1)$ and $h_b(2)$ can be denoted $1s_a(1)$, $2s_a(1)$, $2p_{za}(1)$, ... and $1s_b(2)$, $2s_b(2)$, $2p_{zb}(2)$, ..., respectively, and the restriction that $Z_a \neq Z_b$ assures that the simple product eigenfunctions of H_0 below the solution $2s_a(1)2s_b(2)$ will all be nondegenerate. We choose $Z_a = 2$, $Z_b = 1.9$ so that the three lowest-lying eigenfunctions of H_0 are

$$\Phi_0(1s^2) = 1s_a(1)\, 1s_b(2) \,, \tag{5a}$$

$$\Phi_0(1s2s\,{}^3S) = 1s_a(1)\, 2s_b(2) \,, \tag{5b}$$

$$\Phi_0(1s2s\,{}^1S) = 2s_a(1)\, 1s_b(2) \,, \tag{5c}$$

corresponding to the ground state and first two excited states of He, and the two $1s3s$ zeroth-order eigenfunctions are taken analogously. This choice of Z_a, Z_b is special in that the energy eigenvalues and the expectation values of H for the two $1s2s$ solutions are lower than those for the two $1s3s$ solutions, which is likely to be a necessary condition for convergence of the two expansions. Although the zeroth-order approximation to the ground state is almost symmetric, the expectation value of $\frac{1}{2}(1+P)$ being 0.998, that for the excited triplet is far from being antisymmetric and that for the excited singlet is far from being symmetric, both having expectation values of $\frac{1}{2}(1 \pm P)$ of 0.500. Notice that while the singlet-triplet splitting is no longer given by the simple expression (2), but rather by the more complicated sum of orbital energy differences and expectation values of the perturbation

$$H_1 = 1/r_{12} + (Z_a - 2)/r_1 + (Z_b - 2)/r_2 \,, \tag{6}$$

which supports no simple physical interpretation, the J_1 so obtained is only 30% smaller than the exact value.

We have calculated the perturbation theoretic wave functions and energies to 19th order in H_1 using the technique applied by Riley and Dalgarno[17] to the ground state of He. The procedure employs a 100-term basis set

$$\{\varphi\} = r_1^n r_2^m r_{12}^k \, e^{-\alpha r1 - \beta r2} \tag{7}$$

for $\alpha = 0.75$, $\beta = 2.0$, and $\alpha = 2.0$, $\beta = 0.75$, chosen after a brief search as most suitable for the $1s2s$ solutions, and where n, m, and k are 50 triples of integers. The procedure diagonalizes H_0 in the finite basis so that the coefficient of each of these new functions ξ_i in each perturbed function is obtained without the solution of coupled algebraic equations, e.g.,

$$\Phi_1 = {\sum_i}' \,|\xi_i\rangle \langle \xi_i | H_1 | \Phi_0 \rangle (E_0 - \epsilon_i)^{-1} \,, \tag{8}$$

where ϵ_i are the diagonalized energy values. The calculations were carried out on the twin CDC 6600 system of Sandia Laboratories.

III. RESULTS AND DISCUSSION

The calculated energies are given order by order for the $1s2s\,{}^1S$ and $1s2s\,{}^3S$ states in Table I along with the expectation values of $\frac{1}{2}(1 \pm P)$ and the partial sums are plotted in Fig. 1, where the energies are given in a.u. Convergence is reasonably rapid and even if the calculations were taken only through second order the triplet- and singlet-state errors would be only 0.1 and 0.3%, respectively, and the singlet-triplet splitting in error by 30%.

The convergence of the solutions is best examined by considering the differences $E_n - E_{n-1}$ plotted in Fig. 2. For the ground state these differences seem to converge exponentially, for the $1s2s\,{}^1S$ state the differences oscillate with no clear trend, while for the $1s2s\,{}^1S$ state the differences lie on an almost exactly straight line. The implications of the results through 19th order are thus that the ground state converges quite definitively, that the first excited singlet might converge in some oscillatory way, and that the excited triplet might even

TABLE I. Perturbation energies and expectation values. The energies are the correction terms in each order while the expectation values are those of the normalized wave function to the given order.

	$\Phi(1s2s\,^3S)$		$\Phi(1s2s\,^1S)$	
n	E_n	$\langle\frac{1}{2}(1-P)\rangle^{(n)}$	E_n	$\langle\frac{1}{2}(1+P)\rangle^{(n)}$
0	−2.451 250	0.4996	−2.305 000	0.5004
1	0.354 061	0.6836	0.226 784	0.7917
2	−0.075 244	0.7643	−0.074 426	0.7689
3	0.007 799	0.8223	−0.003 079	0.7980
4	−0.003 119	0.8715	0.004 547	0.8543
5	−0.001 494	0.9093	0.783×10^{-3} [a]	0.9033
6	-0.783×10^{-3} [a]	0.9375	−0.860	0.9333
7	−0.866	0.9580	0.404	0.9509
8	−0.831	0.9727	1.315	0.9643
9	−0.678	0.9828	1.075	0.9759
10	−0.659	0.9896	0.467	0.9844
11	−0.593	0.9940	0.281	0.9900
12	−0.465	0.9968	0.454	0.9935
13	−0.396	0.9984	0.525	0.9960
14	−0.332	0.9993	0.372	0.9977
15	−0.272	0.9998	0.209	0.9988
16[b]	−0.218	0.9999	0.173	0.9994
17	−0.165	0.9999	0.190	0.9997
18	−0.126	0.9999	0.158	0.9999
19	−0.088	0.9998	0.085	1.0000

[a] The 10^{-3} is to be understood for all the higher terms in the table.

[b] The energies through 16th order are −2.175 242 and −2.145 972 which agree with the diagonalized solutions to 0.6×10^{-5} and 1×10^{-5}, respectively, which are the closest that either series agrees with the exact solution within the given basis.

have an asymptotic expansion were the plot to remain essentially linear with $E_n - E_{n-1}$ going through zero at $n = 26$ as indicated in the figure. Such asymptotic behavior would not be surprising but it is of course impossible to distinguish between the observed linear behavior and the beginning of a very slowly oscillating function. Notice that the expectation value of $\frac{1}{2}(1-P)$ "turns around" at $n = 19$, but this can be attributed to accumulated roundoff errors and incompleteness of the basis set as well as to any lack of absolute convergence. The smoothness of the convergence of $\frac{1}{2}(1 \pm P)$ and of the energy for the triplet state should be evidence for the completeness of the basis set sufficient to give two or three decimal places in the energy for the latter.

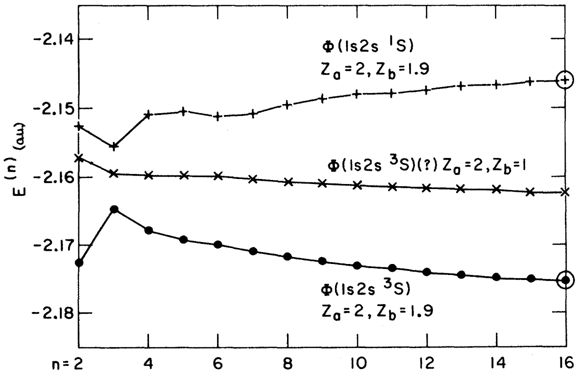

FIG. 1. Partial sums $E^{(n)}$ of the energy for three series as indicated. The circled values coincide with the exact values. The energy is in a.u.

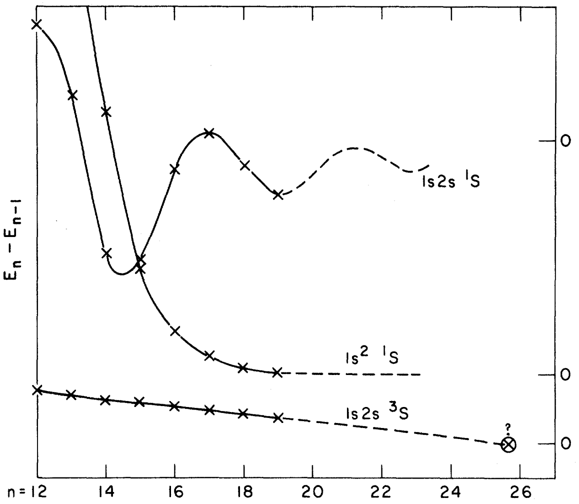

FIG. 2. Energy differences for three series as indicated on an arbitrary scale whose zero is given on the right-hand side. The circled point marked (?) indicates the onset of the divergence if the plot is extrapolated linearly and if an asymptotic expansion is assumed.

The total energies through 19th order are presented in Table II for the four lowest states along with the results of diagonalization of the total Hamiltonian within the finite basis and the best calculated values.[18] The ground state is in error by $< 3\times10^{-9}$, while both $1s2s$ solutions are in error by 0.02% and the $1s3s\,^3S$ solution is in error by 0.16%. The $1s3s\,^1S$ solution diverges and this is presumably due to the fact that the zeroth-order energy and the expectation value of H of the

TABLE II. Helium atom energies in a.u.

	$\Phi(1s^2\,^1S)$ [a]	$\Phi(1s2s\,^3S)$ [b]	$\Phi(1s2s\,^1S)$ [b]	$\Phi(1s3s\,^3S)$ [b]	$\Phi(1s3s\,^1S)$ [b]
$E^{(19)}$	−2.903 67	−2.175 63 [c]	−2.145 54	−2.064 29	... [d]
E_{diag}	−2.903 67	−2.175 23	−2.145 95	−2.067 41	−2.057 29
E_{exact}	−2.903 72	−2.175 23	−2.145 97	−2.068 69	−2.061 27

[a] In basis with $\alpha, \beta = 2.0, 1.0$. The result has converged to the indicated accuracy in ninth order.

[b] In basis with $\alpha, \beta = 2.0, 0.75$.

[c] If the series is assumed to be asymptotic, then the extrapolated "best" value is −2.175 60.

[d] This solution begins to diverge by fourth order.

$1s_a(1)4s_b(2)$ solution are *lower* than that of the $3s_a(1)1s_b(2)$ solution. The expection values of the perturbation theory solutions to different order presumably do not cross if the expansion converges; therefore this $1S_a(1)4s_b(2)$ solution would have to converge to the $1s3s\ ^1S$ solution. The fact that it does not should not be considered surprising in view of the different nodal behavior of the zeroth-order orbitals.

In order to examine further the nature of the convergence of nonsymmetric expansions, we have performed the same set of calculations for the case of $Z_a = 2$, $Z_b = 1$ for which the $1s_a(1)3s_b(2)$ solution has lower energy than the $2s_a(1)1s_b(2)$ solution. The ground-state solution converges to the exact value (-2.90351 a. u. in this basis) by 12th order although the terms from E_{14} through E_{19} oscillate about $\pm 10^{-7}$. The second solution whose partial energy sums are shown in Fig. 1 and which gives $E^{(19)} = -2.16282$ a. u. shows a near-linear $E_n - E_{n-1}$ plot similar to that of Fig. 2 which goes through zero at $n = 25 \pm 3$ with extrapolated value of $E = -2.1637$ a.u. However the plot of $\langle \frac{1}{2}(1-P)\rangle$ which gives 0.6700 in 19th order is almost exactly linear from 5th through 19th order with a slope of 0.0001 and with the 19th order contribution 0.0081. Curiously enough such a series would converge to 1.0028 (in 99th order) and this might well be indicative of the eventual convergence of the series. In any case, the energy through 19th order is definitely not converging with the last term being -1.7×10^{-4} and the last difference being 4×10^{-6}, but such a slowly convergent series could well give a result close to the exact by 100th order. Notice the possibility that the series does not converge but rather oscillates about some average of the $1s2s$ singlet and triplet solutions cannot be ruled out, but that the convergence of the $\langle \frac{1}{2}(1-P)\rangle$ expansion makes it seem rather unlikely.

The third solution gives $E^{(19)} = -2.06483$ a. u., a reasonably good result were it to be associated with the $(1s3s\ ^3S)$ solution, violating the noncrossing rule. However, although the E_{19} is only -1.7×10^{-4} a.u. the corrections have been *increasing* slowly since 9th order so that the convergence should be suspect.

These results show that perturbation expansions for excited states cannot be trivially assumed to give convergent results in accord with previous work.[1,2] The ordering of the energies through first order does play an important role in determining the convergence but it is not necessarily possible to assign *a priori* convergence or divergence of a given expansion. The behavior of the $(1s3s\ ^1S)$ solution of the $Z_a = 2$, $Z_b = 1$ problem illustrates the way an accurate result can be obtained in a series which is possibly divergent. Similar behavior is expected in nonprojected perturbative calculations on intermolecular forces. Such calculations can thus give good results even though the perturbation series will either diverge or converge to an incorrect solution.[19]

IV. CONCLUSIONS

The results of the high-order perturbation-theory calculation show that nonsymmetric functions Φ_0 can indeed be corrected perturbatively to solutions having the correct permutational symmetry. As it seems reasonable to expect that many-electron systems will behave in an analogous manner, we infer that as long as appropriate caution is exercised in the choice of Φ_0 and H_0 one should be able to obtain justifiably good results for many-electron systems based on nonsymmetric Hamiltonians.[9,10] The use of such nonsymmetric Hamiltonians, e. g., the Hartree Hamiltonian, can greatly reduce the computational labor involved in accurate calculations by eliminating large sets of cross terms in the correlated functions as can be seen explicitly in Ref. 11. When, however, a small number such as a singlet-triplet splitting is itself the quantity of interest, although it *can* be calculated as in the present paper, it will generally be preferable to use a method which possesses the correct permutational symmetry for the outside two electrons which give rise to that splitting, while retaining the nonsymmetrical function for all the inner electrons.[9]

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Fermi-Gas Model of the Kapitza Resistance between a Solid and Liquid He^3

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We present a simple Fermi-gas model for the low-temperature Kapitza resistance (KR) of a nonmagnetic liquid-He^3—solid interface in which the vibrational quanta of the solid surface atoms are carried away by single fermion states. A one-dimensional calculation of the energy-exchange process is made assuming that a fermion interacts with a single solid atom through a Morse potential. For temperatures T small compared to the Fermi temperature T_F, the KR R, is found to be of the form

$$RT^3 = a_0 \Big/ \left\{ 1 + \left[46 \left(\frac{k_f}{a} \right)^2 - 1.8 \right] \left(\frac{T}{T_F} \right)^2 \right\},$$

where k_F denotes the Fermi wave vector and a the inverse range parameter of the Morse potential. The constant of proportionality a_0 is generally independent of the nature of the fermion—solid-atom interaction potential and depends on the properties of the Fermi gas only through its dependence on the fourth power of k_F. As a function of increasing T, RT^3 decreases rapidly on account of the largeness of the $(T/T_F)^2$ correction. The theoretical results can therefore account for the pressure and temperature dependences of the KR of the liquid-He^3—copper interface observed by Anderson *et al.* The success of the model tentatively suggests that in the phenomenon of the liquid-He^3 KR, the vibrational quanta of the surface atoms are carried away by individual quasiparticle states rather than by the zero-sound modes considered in the acoustic mismatch theory of Bekarevich and Khalatnikov.

I. INTRODUCTION AND SYNOPSIS

At the present time the only experimental studies of the Kapitza thermal boundary resistance[1] R between a normal Fermi liquid and a simple *monatomic solid* are those of Anderson, Connolly, and Wheatley,[2] Zinovyeva,[3] and the earlier and higher-temperature data of Lee and Fairbank.[4] In these experiments the monatomic solid under study was copper. There are several definitive features of the Kapitza resistance (KR) data, which for the convenience of the reader are reproduced in Figs. 1 and 2. In Fig. 1, RT^3 has been plotted vs the absolute temperature T for the various liquid-He^3 pressures investigated by Anderson *et al.*, and in Fig. 2 the $1/R$ data of Zinovyeva has been plotted vs T. The salient features of the data are the following: (a) For a given liquid-He^3 pressure (density), $R \propto T^{-3}$ at the lowest temperatures, where the appropriate constant of proportionality $a_0 = RT^3$ is of the order of 10^{-5} $cm^2 sec\,deg/erg$ in the experiments of Anderson *et al.* but is some five times smaller in the work of Zinovyeva. (b) As the pressure of liquid He^3 is increased from 1 to approximately 395 lb/in.^{2}, Anderson *et al.* observe that a_0 decreases by a factor close to 1.6. (c) Anderson *et al.*[2] find that at a temperature $T_0 \simeq 0.12$ °K the product RT^3 abruptly begins to decrease with increasing T, where T_0 is, within the experimental error, independent of liquid-He^3 pressure. In contrast, Zinovyeva[3] finds an increase beginning at $T \simeq 0.2$ °K.

The experimental findings of Anderson *et al.*[2] have been compared by them and by Gavoret[5] with the theoretical predictions of the acoustic mismatch theory of Bekarevich and Khalatnikov[6] and of Gavoret.[5] In the acoustic mismatch theory of the latter authors, sound energy from the solid is considered to be transferred at the interface to the collective zero-sound modes[7] of the Fermi liquid. It was found that while the acoustic mismatch theory correctly predicted the limiting low-temperature