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Accurate Perturbative Calculations for the Lithium Atom Based on the Hartree H_0[†]

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Perturbative calculations are carried out to obtain eigenvalues of the four lowest-lying eigenfunctions of the Hartree Hamiltonian for the Li atom through third order in electron correlation. The expansions are all reasonably convergent and the theoretical analysis concerning the possibility of using zeroth-order functions which do not possess the exact permutational symmetry is confirmed in this particular case.

I. INTRODUCTION

The initial proposal of Hartree[1] describing the atomic orbital motion of each electron in the average field of the remaining electrons was early modified to the now widely used Hartree-Fock method[2, 3] in order to include electron spin and the antisymmetry required by Fermi-Dirac statistics. It is, however, possible to use the original Hartree product as the zeroth-order function in a perturbative calculation for a spatial eigenfunction of the exact Hamiltonian from which the exact wave function can be obtained by projection. The procedure, which has been described by Musher and Silbey,[4,5] relies on the fact that the Hartree product function Φ_0 is a nondegenerate spatial eigenfunction of an H_0 which is not symmetric in all the electron indices, i.e.,

$$[H_0, P] \neq 0 \quad \text{all } P \in S_n \ ,$$

so that the various permutations of Φ_0 need not be mixed in zeroth order. Its utility rests on the supposition that perturbation theory can, nevertheless, be relatively rapidly convergent, and that the correct permutation symmetry, which is necessarily built in as the expansion converges, takes care of itself. The present study performs the first calculation using this procedure for a many-electron (i.e., $N > 2$) system. Studies on the electromagnetic properties of the hydrogen molecule[6-8] and on the lowest excited states of the He atom[9] have shown that for two-electron systems such convergence is indeed obtained.

II. PROCEDURE

The Hartree spatial orbital product for the ground-state Li atom is

$$\Phi_0 = 1s_a(1)\,1s_a(2)2s_b(3) \equiv a(1)\,a(2)\,b(3)\ , \tag{1}$$

where the orbitals a and b are the lowest and second lowest self-consistent eigenfunctions, respectively, of the equations

$$[h_a(i) - \epsilon_k^a\,]\,a_k(i) = 0, \quad i = 1, 2 \tag{2a}$$

and

$$[h_b(3) - \epsilon_k^b\,]\,b_k(3) = 0\ . \tag{2b}$$

The Hamiltonians are defined by

$$h_a(i) = -\tfrac{1}{2}\nabla_i^2 - 3/r_i + V_a(i), \quad i = 1, 2 \tag{3a}$$

and

$$h_b(3) = -\tfrac{1}{2}\nabla_3^2 - 3/r_3 + V_b(3)\ , \tag{3b}$$

with

$$V_a(i) = [-a|-a]_i + [-b|-b]_i\ , \quad i = 1, 2 \tag{4a}$$

and

$$V_b(3) = 2[-a|-a]_3 \tag{4b}$$

constructed from the self-consistent orbitals

$$a \equiv a_1 \equiv 1s_a$$

and

$$b \equiv b_2 \equiv 2s_b\ ,$$

so that electrons 1 and 2 are in the Coulomb field of one 1s and one 2s electron, and electron 3 is in the Coulomb field of two 1s electrons; there are no exchange fields in the definition of the problem.

The Hartree function Φ_0 is an eigenfunction of the zeroth-order Hamiltonian

$$H_0 = h_a(1) + h_a(2) + h_b(3)\ , \tag{5}$$

which is symmetric under the permutation P_{12} but has no symmetry under any of the four remaining nontrivial permutations of S_3. This H_0 generates a complete set of orthogonal eigenfunctions $a_i(1)\,a_j(2)\,b_k(3)$ all of which can be used as zeroth-order eigenfunctions in a perturbative scheme. We thus consider here not only the perturbative expansion based on the Hartree function (1) but also the perturbative expansions for three other low-lying spatial functions. In particular we will deal with the four perturbation-theoretic expansions

$$\Phi_1^1(1s^3) = \Phi_0^{1,1}(1s^3) + \lambda\Phi_1^{1,1}(1s^3) + \ldots , \tag{6a}$$

$$\Phi_1^2(1s^2\,2s) = \Phi_0^{2,1}(1s^2\,2s) + \lambda\Phi_1^{2,1}(1s^2\,2s) + \cdots , \tag{6b}$$

$$\Phi_2^2(1s^2\,2s) = \Phi_0^{2,2}(1s^2\,2s) + \lambda\Phi_1^{2,2}(1s^2\,2s) + \cdots , \tag{6c}$$

and

$$\Phi_1^1(1s^2\,2s) = \Phi_0^{1,1}(1s^2\,2s) + \lambda\Phi_1^{1,1}(1s^2\,2s) + \cdots , \tag{6d}$$

where

$$\Phi_0^{1,1}(1s^3) = a_1(1)\,a_1(2)\,b_1(3) , \tag{7a}$$

$$\Phi_0^{2,1}(1s^2\,2s) = a_1(1)\,a_1(2)\,b_2(3) \equiv a(1)\,a(2)\,b(3) , \tag{7b}$$

$$\Phi_0^{2,2}(1s^2\,2s) = 2^{-1/2}(1 - P_{12})\,a_1(1)\,a_2(2)\,b_1(3) , \tag{7c}$$

and

$$\Phi_0^{1,1}(1s^2\,2s) = 2^{-1/2}(1 + P_{12})\,a_1(1)\,a_2(2)\,b_1(3) . \tag{7d}$$

The notation, which we have attempted to make as simple as possible despite the inherent complexity of the problem, indicates the representations of S_3 characterized by partitions [3], [2, 1], and [1^3], denoted by the indices 1, 2, and 3, respectively, which are given as superscripts on the exact functions and the first superscript on the approximate functions. The rows of the irreducible orthogonal representation according to which the exact functions are to transform are indicated by the subscript on the exact function and the second superscript on the approximate functions with numbering used earlier,[5] i.e., 1 refers to the unique row of representations 1 and 3 (not used here) and 1 and 2 refer to the rows of representation 2 which are symmetric and antisymmetric, respectively, under P_{12}. The $1s^3$ and $1s^2\,2s$ indicate the "configuration" to which the solution belongs and are actually unnecessary for Φ_1^2 and Φ_2^2, there being no solutions of this symmetry in $1s^3$. Analogous expansions can be written for the energy eigenvalues, e.g.,

$$E_1^2(1s^2\,2s) = E_0^{2,1} + \lambda E_1^{2,1} + \lambda^2 E_2^{2,1} + \lambda^3 E_3^{2,1} + \cdots , \tag{8}$$

and our calculations are carried out to the order indicated, i.e., the eigenfunctions are calculated through first order and the eigenvalues through third order.

The eigenfunctions $\Phi_1^1(1s^3)$ and $\Phi_1^1(1s^2\,2s)$ being totally symmetric in the electron indices have no physical significance while the two eigenfunctions Φ_1^2 and Φ_2^2 must be combined with the conjugate spin functions

$$\chi_1^{\tilde{2}} = \chi_2^2 = 2^{-1/2}(\alpha\beta\alpha - \beta\alpha\alpha) , \tag{9a}$$

$$\chi_2^{\tilde{2}} = \chi_1^2 = 6^{-1/2}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) \tag{9b}$$

to give the actual wave function for the ground state of the Li atom

$$\Psi(r, \sigma) = \sum_{i=1}^{2} \Phi_i^2(r)\,\chi_i^{\tilde{2}}(\sigma) , \tag{10}$$

assuming the appropriate phase convention. For our purposes, however, there is no need to construct the wave function $\bar{\Psi}(r, \sigma)$ since the electronic Hamiltonian is spin independent.[10] The two solutions Φ_i^2 will therefore be degenerate even though the calculated eigenvalues will never be exactly equal at any finite order in the perturbation expansion, and thus the expansion based on the Hartree product $\Phi_0^{2,1}$ would have been sufficient for the present problem if we were not interested in the general behavior of the other solutions which should be presented at least this once.

The perturbation-theoretic calculation is carried out by writing the perturbation

$$\lambda H_1 \equiv H - H_0 = g_{aa}(12) + (1 + P_{12})\,g_{ab}(13) , \tag{11}$$

with the pair-perturbations

$$g_{aa}(12) = 1/r_{12} - \tfrac{1}{2}[V_a(1) + V_a(2)] \tag{12a}$$

and

$$g_{ab}(13) = 1/r_{13} - \tfrac{1}{2}[V_a(1) + V_b(3)] , \tag{12b}$$

which were denoted by $g'(ij)$'s in Ref. 4. The four first-order functions are

$$\Phi_1^{1,1}(1s^3) = U_{a1a1}(12)\,b_1(3) + (1 + P_{12})\,U_{a1b1}(13)\,a_1(2) , \tag{13a}$$

$$\Phi_1^{2,1}(1s^2\,2s) = U_{a1a1}(12)\,b_2(3) + (1 + P_{12})\,U_{a1b2}(13)\,a_1(2) , \tag{13b}$$

$$\Phi_1^{2,2}(1s^2\,2s) = 2^{-1/2}(1 - P_{12})\,Q(123) , \tag{13c}$$

$$\Phi_1^{3,1}(1s^2\,2s) = 2^{-1/2}(1 + P_{12})\,Q(123) , \tag{13d}$$

with

$$Q(123) = U_{a1a2}(12)\,b_1(3) + a_1(1)\,U_{a2b1}(23) + U_{a1b1}(13)\,a_2(2) , \tag{14}$$

where the five pair functions are solutions to two-particle inhomogeneous partial differential equations, e.g.,

$$[h_a(1) + h_b(2) - \epsilon_1^a - \epsilon_2^b]\,U_{a1b2}(12) = [\langle a_1 b_2 | g_{ab} | a_1 b_2\rangle - g_{ab}(12)]\,a_1(1)\,b_2(2) . \tag{15}$$

The self-consistent eigenvalue equations were solved numerically and the eigenvalues of interest are

$$\epsilon_1^a = -2.4924 , \quad \epsilon_1^b = -1.2275 , \quad \epsilon_2^a = -0.3221 ,$$

and

$$\epsilon_2^b = -0.1761 .$$

(The energies are given in atomic units, a.u., throughout the article.) Notice that the spectra of h_a and h_b are very different, as expected, but that the two $1s$ functions have very similar spatial behavior since $\langle a_1 | b_1\rangle \sim 0.98$. The solution to the two-particle equations were accomplished by partial wave expansions and the numerical integration of the resultant equations[11] on a two-dimensional grid with mesh $h = 0.2$ a.u. for $0 \leqslant r_1, r_2 \leqslant 20$ using a method similar to that of Schulman and Lee.[12]

The second- and third-order energies for the Hartree state are simple relative to the more complicated way of treating total wave functions and are given by

$$E_2^{2,1} = \langle a_1(1)\, a_1(2)\, b_2(3)\ |g_{aa}(12) + (1+P_{12}) g_{ab}(13) - E_1^{2,1}\,|\, U_{a1a1}(12)\, b_2(3) + (1+P_{12})\, U_{a1b2}(13)\, a_1(2) \rangle \tag{16}$$

and

$$E_3^{2,1} = \langle U_{a1a1}(12)\, b_2(3) + (1+P_{12})\, U_{a1b2}(13)\, a_1(2)\ |g_{aa}(12) + (1+P_{12}) g_{ab}(13) - E_1^{2,1}\,|\, U_{a1a1}(12)\, b_2(3) + (1+P_{12})\, U_{a1b2}(13)\, a_1(2) \rangle - 2E_2^{2,1} \langle a_1(1)\, a_1(2)\, b_2(3)\,|\, U_{a1a1}(12)\, b_2(3) + (1+P_{12})\, U_{a1b2}(13)\, a_1(2) \rangle\ . \tag{17}$$

A number of integral identities serve to test the accuracy of these numerical pair functions and the subsequent integrations. These expressions are given in the Appendix and suggest that the numerical errors are rather small.

III. RESULTS

The "energy" eigenvalues calculated through third order for the various solutions are presented in Table I where, of course, the "energies" of the symmetric solutions $\Phi_1^1(1s^3)$ and $\Phi_1^1(1s^2 2s)$ are nonphysical. As can be seen, the convergence is relatively rapid for all of the expansions with the $E_1^2(1s^2 2s)$ and $E_2^2(1s^2 2s)$ rapidly approaching each other and bracketing the exact value of -7.47807 with errors of -0.017 or 0.2% and $+0.009$ or 0.1%, respectively. If correlation energy is defined as the difference between E_{exact} and $E^{(1)}$ for *each* of these expansions then these results give 74 and 95% of the correlation energy, respectively. It appears that the "energy" $E_1^1(1s^2 2s)$ is converging to a value higher than that for the degenerate physical eigenvalues consistent with the expectation from the generalized Hund's rule,[4,5] although it would be desirable to have still higher-order calculations to check this further. The generalized Hund's rule says, in effect, that for several solutions belonging to a given configuration the "higher" the symmetry of a solution the higher will be its eigenvalue. Thus, just as the energy of a singlet is higher than that of a triplet, the "energy" of a still more symmetrical spatial function (for which there is no spin counterpart for the construction of a wave function) will be higher still.

It is anticipated that the expectation values of the symmetry projection operators[5] D_{ii}^{α} will converge to unity as the perturbation expansion converges, but for the Hartree problem in which we are most interested

$$\langle \Phi_0^{2,1} \,|\, D_{11}^2 \,|\, \Phi_0^{2,1} \rangle = 0.662$$

and

$$\frac{\langle \Phi_0^{2,1} + \Phi_1^{2,1} | D_{11}^2 | \Phi_0^{2,1} + \Phi_1^{2,1} \rangle}{\langle \Phi_0^{2,1} + \Phi_1^{2,1} | \Phi_0^{2,1} + \Phi_1^{2,1} \rangle} = 0.682\ .$$

It thus appears that first order is not accurate enough to obtain any sense of this convergence, and this is similar to the behavior noted in the nonsymmetric calculations on the excited states of the He atom[9] where it was found that smooth convergence of the symmetry projectors was only obtained in the high orders of the expansion. The analogous expectation values of D_{22}^2 in zeroth and first order are 0.995 and 1.085, respectively. These latter values are strikingly better than the Hartree ones, since a significant amount of the correct symmetry is already built into the problem in zeroth order due to the $2^{-1/2}(1-P_{12})$ in the $1s^2 2s$ solution.

The present calculation provides an energy for the Li atom of -7.4610 based on introducing electron correlation perturbatively into the Hartree simple-product spatial function. The calculations on the other solutions show that the arguments on the convergence of the set of expansions based on nonsymmetrical zeroth-order spatials are, at least, not contradicted in this one simple example. The perturbed Hartree calculation is not intended to compete with the various more accurate

TABLE I. Perturbation "energies" of lithium for several spatial eignefunctions. $E^{(n)} = \sum_{i=0}^{n} E_i$, energies in atomic units (a.u.).

	$\Phi_1^1(1s^3)$		$\Phi_1^2(1s^2 2s)$		$\Phi_2^2(1s^2 2s)$		$\Phi_1^1(1s^2 2s)$	
n	E_n	$E^{(n)}$	E_n	$E^{(n)\text{a}}$	E_n	$E^{(n)\text{a}}$	E_n	$E^{(n)}$
0	−6.2124	−6.2124	−5.1610	−5.1610	−4.0420	−4.0420	−4.0420	−4.0420
1	−4.5767	−10.7891	−2.2513	−7.4123	−3.2585	−7.3005	−3.1778	−7.2198
2	−0.1619	−10.9510	−0.0547	−7.4670	−0.2118	−7.5123	−0.2017	−7.4215
3	+0.1486	−10.8024	+0.0060	−7.4610	+0.0256	−7.4867	−0.0072	−7.4287

[a] $E(\text{expt}) = -7.47807$. C. W. Scherr, N. J. Silverman, and F. A. Matsen, Phys. Rev. <u>127</u>, 5343 (1967).

calculations that have been carried out for the simple case of the Li atoms,[12,13] but the application of this procedure is expected to find utility in calculations on many-electron systems and particularly on molecules for which the simplicity afforded by the elimination of the many cross and exchangelike terms will be most valuable. Thus the rapid convergence of the expansion is gratifying, even though the relative error of 0.2% is larger than that of many other Li atom calculations, and this augurs well for future calculations on many-electron systems using simple product Φ_0's. Further investigative work will, of course, be necessary, but it does seem reasonable to conclude that the inclusion of electron correlation into a Hartree product function can provide accurate energy eigenvalues and that the explicit introduction of the exact permutational symmetry or "electron exchange" is not required in accord with the theoretical arguments.[4,5]

APPENDIX

As in Ref. 9 there are a number of ways of expressing overlap integrals between pair functions and orbitals in terms of two electron integrals involving solely orbitals, those latter integrals being amenable to accurate evaluation. Some of these identities are given here with the numerical value of the integral given below the symbolic expression:

$$\langle a_1 a_2 | U_{a1a1}\rangle = \langle a_2 b_2 | U_{a1b2}\rangle = -\langle a_1 a_1 | U_{a1a2}\rangle$$

$$0.04577 \qquad 0.04514 \qquad 0.04448$$

$$= \frac{\tfrac{1}{2}\{[a_1 b_2 | a_2 b_2] - [a_1 a_2 | a_1 a_1]\}}{\epsilon_2^a - \epsilon_1^a}, \tag{A1}$$

$$0.04499$$

$$\langle a_2 a_2 | U_{a1a1}\rangle = \frac{\tfrac{1}{2}[a_2 a_2 | a_1 a_1]}{\epsilon_1^a - \epsilon_2^a}, \tag{A2}$$

$$-0.009124 \qquad -0.009288$$

$$\langle a_2 b_1 | U_{a1b2}\rangle = -\langle b_2 a_1 | U_{b1a2}\rangle$$

$$-0.02770 \qquad -0.02764$$

$$= \frac{-[a_2 b_1 | a_1 b_2]}{\epsilon_2^a + \epsilon_1^b - \epsilon_1^a - \epsilon_2^b}, \tag{A3}$$

$$-0.02639$$

$$\langle a_2 a_2 | U_{a1a2}\rangle = \frac{\tfrac{1}{2}\{\langle a_1 | V_a | a_2\rangle - [a_2 a_2 | a_2 a_1]\}}{(\epsilon_2^a - \epsilon_1^a)}, \tag{A4}$$

$$-0.04215 \qquad -0.04192$$

$$\langle a_1 b_1 | U_{a1b1}\rangle = -[b_1 b_1 | U_{b1a2}]$$

$$0.02618 \qquad 0.02574$$

$$= \frac{\tfrac{1}{2}\{\langle a_1 | V_a | a_1\rangle - [a_1 b_1 | a_2 b_1]\}}{\epsilon_2^a - \epsilon_1^a}, \tag{A5}$$

$$0.02778$$

$$\langle a_2 b_2 | U_{b1a2}\rangle = \frac{-[a_1 b_1 | a_2 b_2]}{\{\epsilon_2^a - \epsilon_1^a + \epsilon_2^b - \epsilon_1^b\}}, \tag{A6}$$

$$-0.00850 \qquad -0.00916$$

$$\langle b_2 a_2 | U_{b12a}\rangle = \frac{\tfrac{1}{2}\{\langle b_2 | V_b | b_1\rangle - [b_2 a_2 | b_1 a_1]\}}{\epsilon_2^b - \epsilon_1^b}. \tag{A7}$$

$$-0.1415 \qquad -0.1470$$

Notice that the function of relation (A3) is less than 1 as was shown in Ref. 4 [Eq. (44)] to be a necessary condition for perturbation theory to converge.

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