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Variational Calculation on Muonic Molecules*

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Hylleraas-type trial functions with up to $N=120$ terms are used in a variational calculation of several bound S states of muonic molecules. The convergence of the energy levels with increasing N is investigated.

I. INTRODUCTION

THE form of trial function used by Hylleraas[1] and Pekeris[2] on the helium-atom ground state has been applied to the ground states of two muonic molecules by Kolos, Roothaan, and Sack[3] who used a 32-term trial function. Their results for $p\mu p$ and $d\mu d$ were far less accurate than a calculation of the He ground state with a comparable number of terms. Partly because of this difficulty, most of the more recent variational calculations of the S states of muonic molecules[4,5] have been performed using other, radically different trial functions in place of the Hylleraas type. An exception is the calculation by Frost, Inokuti, and Lowe,[4] who used Pekeris's series method[2] with an 84-term trial function similar to that of Ref. 3.

In the present work, we investigate the convergence of variational calculations of several muonic molecule S states, with increasing number of terms N. We use a well-defined sequence of Hylleraas-type trial functions (described in Sec. II) as advocated by Schwartz.[6] This is in contrast to the procedure of determining by trial-and-error which terms are most important for a given N. The point is that we are interested in the asymptotic behavior for large N (for which the former procedure has fewer pitfalls) rather than the question of how well we can do with a given small value of N.

A generalization of the Hylleraas type of trial function was used in Ref. 3, and a different generalization was attempted by us. Both are described in Sec. II of this paper, along with the trial functions which we finally adopted. Our numerical results are also presented in Sec. II.

Section III contains a discussion of the convergence of our computed energy levels with increasing N, and a comparison with previous calculations in the literature.

II. TRIAL FUNCTIONS AND ENERGY LEVELS

The Hylleraas type of trial function[1] is

$$\psi=\exp(-\alpha r_{13}-\alpha r_{23})P_N(r_{12},r_{13},r_{23})\,, \qquad (1)$$

where r_{ij} is the distance between particles i and j, and P_N is a polynomial. Equation (1) was generalized in Ref. 3, where the trial function employed was

$$\psi=\exp(-\alpha_{12}r_{12}-\alpha_{13}r_{13}-\alpha_{23}r_{23})P(r_{12},r_{13},r_{23})\,. \quad (2)$$

Nevertheless, the best results quoted in Ref. 3 for $p\mu p$ and $d\mu d$ were of the form of Eq. (1), where particles 1 and 2 are the nuclei.[7]

We have tried replacing the exponential in Eq. (2) by a sum of two exponentials, since such a sum gives a good fit[8] to the two-center problem. The result was a slight improvement over Eq. (1) when the polynomial P had 10 to 20 terms, but the improvement rapidly becomes negligible with increasing N. For this reason we shall restrict our attention to trial functions of the Hylleraas type (1) in what follows.

There is still some leeway in the choice of the polynomial P_N in Eq. (1). A standard choice, which we shall follow, is

$$P_N(r_{12},r_{13},r_{23})=\sum_{\substack{i+j+k\leq n\\ i\geq 0,\, j\geq 0,\, k\geq 0}} X_{ijk}r_{12}{}^{i}r_{13}{}^{j}r_{23}{}^{k}\,. \quad (3)$$

The number of terms in the sum above is

$$N=\tfrac{1}{6}(n+1)(n+2)(n+3)\,.$$

The problem of optimizing the X's of Eq. (3) leads to an eigenvalue problem involving N by N matrices, as is well known. In computing the matrix elements recursively, care must be taken[9] to avoid large roundoff errors.

The Hamiltonian of our problem is, in atomic units,

$$H=-\sum_{i=1}^{3}\nabla_i{}^2/2m_i+\sum_{1\leq i<j\leq 3}e_ie_j/r_{ij}\,, \qquad (4)$$

which depends, of course, on the masses (m_i) and charges (e_i) of the particles. The values of these

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[6] C. Schwartz, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2, p. 241.

[7] According to Ref. 3, some advantage was gained in going from (1) to (2) for the cases of the hydrogen molecular ion and the helium atom.

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TABLE I. Masses and charges used in computing energy levels.

Particle	Symbol used in text[a]	Mass (a.u.) m	Charge (a.u.) e
Proton	p	1836.12	$+1$
Deuteron	d	3670.4	$+1$
Triton	t	5496.8	$+1$
Muon	μ	206.77	-1
Electron	$\cdots$	1	-1
He nucleus	$\cdots$	infinity	$+2$

[a] These symbols are also used in Table II. The designations $p\mu p$, etc. for muonic molecules are the ones most frequently found in the literature.

quantities which we have used are shown in Table I. The masses (in units of the electron mass) are known to five or six decimal places. Various values have been used[4,5]; hence a correction must be made in comparing the accuracy achieved in different calculations. The values in Table I agree with those which we have used previously.[5]

A program was written to compute the matrix elements of the Hamiltonian and of unity, and to solve the eigenvalue problem for the energy levels. The program was run on two computers (IBM 7094 and CDC 6600). The results are shown in Table II. Besides the molecular states, the helium ground state was also computed for various N as a check on our program. The exponential parameters were chosen arbitrarily to be $\alpha=2$ for helium, and $\alpha=200$ for muonic molecules. No attempt was made to optimize these values of α.

TABLE II. Energy levels of some S states of three-particle systems.

System	Vibrational quantum number V	Number of terms in trial function N	Binding energy $\|E\|$ (a.u.)
He	0	10	2.902 966
		20	2.903 627
		35	2.903 713 514
		56	2.903 720 328
		84	2.903 722 991
$p\mu p$	0	10	99.1899
		20	101.3307
		35	102.0340
		56	102.2028
		84	102.2188
		120	102.2215
$p\mu d$	0	10	102.85
		20	105.0124
		35	105.7046
		56	105.9693
		84	106.0030
$d\mu d$	0	10	106.4233
		20	108.6308
		35	109.2221
		56	109.6830
		84	109.7879
$d\mu d$	1	10	66.5992
		20	91.7076
		35	96.3343
		56	98.5606
		84	99.0751
$d\mu t$	0	10	107.7247
		20	110.0439
		35	110.5982
		56	111.1563
		84	111.3164
		120	111.3257
$d\mu t$	1	10	68.0439
		20	93.5731
		35	98.1167
		56	100.1500
		84	100.7610
		120	100.8475

III. DISCUSSION OF RESULTS

For each S state which we have calculated, Table II includes a sequence of values (corresponding to different N) for the binding energy $|E|$. Each such sequence is monotonically increasing and presumably converges to the absolute value of an eigenvalue of the Hamiltonian, Eq. (4). From the differences between successive terms in each sequence, some conclusions can be drawn about the convergence rate.

(i) The convergence rate for muonic molecules is slow compared to the rate for the He ground state, at least in the region $N \lesssim 100$.

(ii) The convergence continues to get slower as the reduced mass of the two nuclei increases.

(iii) The convergence is faster for the ground states than for the first vibrationally excited states of muonic molecules.

(iv) As N increases up to about 100, the differences are alternately large and small. For He, large differences are found between $N=20$ and 35, and again between 56 and 84. For muonic molecules, the effect is more pronounced, and large differences are found at the same steps in N that yield small differences for He. The effect is most extreme from 35 to 56, where the difference is greater than that from 20 to 35 for the $d\mu t$ ground state. (With this one exception, the differences in the last column of Table II are monotonically decreasing with N.)

(v) From the irregularity of the differences, we conclude that the values of N in Table II have not yet reached the asymptotic region, where predictions can be made as to the behavior of further terms in the sequence. Nevertheless, each "large" difference is greater than the sum of all the subsequent differences that we have calculated. If the large differences really are greater than the sums of subsequent differences for all N, then our $N=120$ result for $p\mu p$ should be accurate to within 0.0027 a.u., or about 0.07 eV.

Although the aim of this paper was not primarily to compute energy levels with extreme precision, the binding energies in Table II are generally greater than those of previous variational calculations,[4,5] with one exception: Wessel and Phillipson[4] computed a dissociation energy[10] of 254.3 eV for the $p\mu p$ ground state.

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[10] The dissociation energy is the difference between the energy of the $p\mu p$ molecule and that of the $p\mu$ atom. The latter is 2528.4 eV according to Table I (and substituting $1=27.21$ eV). The $p\mu$ energy given by Wessel and Phillipson is consistent with $m_\mu=206.8$ and $1=27.21$ eV.

Corresponding to our $p\mu p$ binding energy in Table II is a dissociation energy of 253 eV. The difference of 1.3 eV is too large to be explained by the difference[10] in values assumed for the muon mass. A satisfactory explanation will have to await further calculations.

For the case of $p\mu d$, the difference between our results and those of Frost, Inokuti, and Lowe[4] may be due to their use of a nonorthogonal set of basis functions. It has been pointed out[11] that the series-recursion method is not always equivalent to a variational calculation, for such a basis.

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Polarization Corrections for Shielding and Antishielding Configurations of the Copper Atom

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The level-crossing technique has been used to measure the hyperfine structure constants of the Cu^{63} nucleus in the $(3d)^{10}4p\ {}^2P_{3/2}$ state. To extract a value for the nuclear quadrupole moment, configuration interaction effects are allowed for by performing a least-squares fit to the energy levels. The value obtained is in serious disagreement with a value for Q inferred from the $(3d)^9(4s)^2$ configuration. The copper moment may therefore serve as a test for Sternheimer or other polarization corrections that must be invoked to explain the discrepancy.

INTRODUCTION

THE phenomenon of configuration interaction has continually plagued efforts to extract values for nuclear moments from hyperfine structure (hfs) data. The problem is especially severe for excited atomic states. Thus, much of the precision of data obtained by modern techniques of optical spectroscopy, including optical and electron pumping, is lost as far as the nuclear moments are concerned. However, the problem is by no means restricted to excited states. Nuclear quadrupole moments deduced from ground-state hfs measurements must be subjected to the so-called Sternheimer correction.[1] This correction and other limited configuration interaction approaches, which we may call polarization corrections, remain in vogue because of the absence of accurate unrestricted Hartree-Fock functions for the great majority of atoms and ions. Polarization corrections are often cast in the form of a perturbation expansion. As such, they may be gradually refined. One such refinement is inclusion of excitations to states of the continuum.[2] Needless to say, unambiguous tests of the various polarization correction schemes would be highly desireable. A determination of a nuclear quadrupole moment from its interaction in two dissimilar electronic configurations, for instance, could constitute a stringent test. Moreover, certain forms of configuration interaction are not tractable in a perturbation approach, or can be treated in a more consistent way by other techniques.

To illustrate these ideas, we discuss below the extraction of the quadrupole moment, Q, of the Cu^{63} nucleus from the measured value of the hyperfine interaction constant in the $(3d)^{10}4p$ configuration. We first show that standard Racah techniques can be used to take the configuration interaction of $(3d)^{10}4p$ with $(3d)^9 4s4p$ into account. The procedure is to deduce the configuration interaction from a least-squares fit to the energies of the observed levels. With the improved electronic wave function so obtained, a value for the nuclear quadrupole moment is inferred. Using this procedure, we find that our measured value $B=-28.75(70)$ Mc/sec implies $Q=-0.315(12)$ b. In a recent optical measurement, the quadrupole constant for Cu^{65} was determined in the $(3\mathrm{d})^9(4s)^2$ configuration.[3] The relevant energy levels are shown in Fig. 1. When this is scaled up by the known ratio of the moments,[4] a value $Q=-0.176(5)$ b is obtained. The size of the discrepancy suggests that copper may provide a sensitive testing ground for polarization corrections to quadrupole moments. It also emphasizes the importance of $d^n \longrightarrow d^{n-1}s$ configuration interaction for hfs. This is neither of the angular nor of the radial type considered by Stern-

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