# Finite-Mass Helium Atoms. I. The 2 ¹P State*

Milos Machacek,† Frank C. Sanders, and Charles W. Scherr

*Physics Department, The University of Texas, Austin, Texas*

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The 2 ¹P states of the helium isoelectronic series are investigated via 50-term variational wave functions containing two nonlinear parameters. The Hamiltonian, spin-free and nonrelativisitic, is written directly in center-of-mass coordinates so that no adiabatic approximation is required. The expectation values of the Hamiltonian and of moments of the interparticle separations are reported. Isotope shifts are found and, as noted in a preliminary report, are in excellent agreement with experiment. In order to compare the results with previous theoretical results, the systems were similarly studied in the infinite-nuclear-mass limit (adiabatic approximation). The energies so obtained are the deepest thus far obtained by a direct calculation with a variational wave function. The expectation values of the operators were subjected to a differencing process to obtain estimates of the perturbation expansion coefficients for them, and the results are in good agreement with the directly calculated results of Knight and Scherr.

## I. INTRODUCTION

THE theoretical treatment of the $P$ states of the two-electron atom has been a subject of interest in the quantum mechanics that starts with the pioneering work of Breit[1] and continues down to the present, e.g., in the work of Pekeris, Schiff, and Lifson.[2] These investigations have always used an infinite-nuclear-mass approximation and have attempted to account for the actual motion of the nucleus by some perturbation technique such as was developed by Hylleraas[3] (Rydberg constant correction) and by Hughes and Eckart[4] (first-order mass polarization correction). For many purposes, this is an entirely adequate mode of procedure. However, occasionally difficulties arise. For example, certain isotope shift effects are too small to be handled by these techniques in first order.[5] Also, there are systems where the masses of the particles are more nearly equal than in ordinary atoms, for example, in the $\mu$-mesonic isotopic hydrogen molecule ion[6] $p^+\mu^-d^+$, or in the interesting but so far hypothetical[7] system of two electrons and a positron, $e^-e^+e^-$. In such systems, the above procedures are obviously inappropriate. Successful attempts to dispense with the infinite-mass approximations have now been made by a number of investigators,[8] usually for states of zero angular momentum.

Scherr and Machacek[9] have made extensive study of systems of three Coulombic particles possessing unit angular momentum in which the mass dependence was rigorously and completely taken into account. Their computer programs have been used here to investigate in more thorough detail the 2 ¹P states of the helium isoelectronic series.

Knight and Scherr[10,11] have investigated the $P$ states of the helium isoelectronic series by a Schrödinger perturbation procedure. This procedure, as is well known, presents a wave function as an expansion in powers of the perturbation expansion parameter—in the helium atom case, inverse powers of the nuclear charge $Z$. Thus,

$$\Psi = \sum Z^{-n}\Psi_n. \tag{1}$$

Consequently, expectation values of operators are also obtained in a power series in $Z^{-1}$

$$\int d\tau \Psi \Omega \Psi \equiv \langle \Omega \rangle = \sum Z^{a-n} \langle \Omega \rangle_{n'}, \tag{2}$$

where the value of $a$ depends on the nature of the operator $\Omega$. The $\Psi$ is assumed to be real and to be normalized for simplicity. In particular, the expectation value of the Hamiltonian is the total energy

$$E = Z^2 \sum Z^{-n} \epsilon_n. \tag{3}$$

It is possible[12,13] to obtain estimates of the leading coefficients in Eqs. (2) and (3) from the results of a series of

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† Present address: 80 Burley Street, Danver, Massachusetts.

[1] G. Breit, Phys. Rev. **35**, 569 (1930).

[2] C. L. Pekeris, B. Schiff, and H. Lifson, Phys. Rev. **126**, 1057 (1962).

[3] E. Hylleraas, Z. Physik **54**, 347 (1929).

[4] D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930).

[5] M. Machacek and C. W. Scherr, J. Chem. Phys. **39**, 3151 (1963).

[6] Cf. J. D. Jackson, Phys. Rev. **106**, 330 (1957).

[7] A proper description of this system cannot be given by a time-independent, nonrelativistic, spin-independent Hamiltonian such as the one employed in this note.

[8] W. Kolos, C. C. J. Roothaan, and R. A. Sack, Rev. Mod. Phys. **32**, 178 (1960); A. Fröman and J. L. Kinsey, Phys. Rev. **123**, 2077 (1961); H. Diehl, S. Flügge, U. Schröder, A. Völker, and A. Weiguny, Z. Physik **162**, 1 (1961); H. Diehl and S. Flügge, *ibid.* **162**, 21 (1961); S. Flügge and U. Schröder, *ibid.* **162**, 28 (1961); U. Schröder, *ibid.* **173**, 221 (1963); S. Cohen, D. L. Judd,

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[9] C. W. Scherr and M. Machacek (unpublished material).

[10] R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 431 (1963).

[11] R. E. Knight and C. W. Scherr (unpublished calculations). These authors regard their $\epsilon_4$ and $\epsilon_5$ data, quoted here, as tentative, and their $\epsilon_6$ value, also quoted here, as open to considerable doubt.

[12] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

[13] C. W. Scherr and J. N. Silverman, J. Chem. Phys. **37**, 1154 (1962).

variational calculations by a procedure referred to as a "differencing technique." These estimates have been obtained from the results reported here, and the comparison with the perturbation results of Knight and Scherr indicates that their first-order results[10] are good; no conclusion can be made about their higher order results. Both the work of Knight and Scherr and the coefficient estimations made here deal with wave functions constructed in the infinite-nuclear-mass approximation. For the perturbation approach to be applied in the true mass calculation, the systems (i.e., He, $Li^+$, $Be^{++}$, etc.) all would be required to have the same nuclear masses. In this way, most of the systems studied would be just as artificial as the infinite-nuclear-mass systems.

## II. PROCEDURE

The wave function employed by Scherr and Machacek has already been briefly described,[5] and a more thorough report will soon appear.[9] Aside from being an eigenfunction of the angular momentum, it is a 50-term expansion with an exponential factor containing two nonlinear parameters. These nonlinear parameters were carefully optimized for the systems with infinite nuclear masses. These same nonlinear parameter values were then used in the variational calculations for the systems with the true nuclear masses.[14] (The 50 linear parameters were, of course, determined each time via the

TABLE I. The energies in reduced atomic units.[a]

| Isotope | $(m/M)\times10^4$ | $E$(true mass) | $E$(infinite mass) |
|---|---|---|---|
| $He^3$ | 1.8192 | $-\ 2.12383358$ | |
| $He^4$ | 1.3706 | $-\ 2.12383565^-$ | $-\ 2.12384195^+$ |
| $Li^6$ | 0.9126 | $-\ 4.99332659$ | |
| $Li^7$ | 0.7821 | $-\ 4.99332987$ | $-\ 4.99334951$ |
| $Be^9$ | 0.6089 | $-\ 9.11073181$ | $-\ 9.11076965^-$ |
| $B^{10}$ | 0.5480 | $-14.4772178$ | |
| $B^{11}$ | 0.4984 | $-14.4772236$ | $-14.4772810$ |
| $C^{12}$ | 0.4573 | $-21.0932455^+$ | |
| $C^{13}$ | 0.4220 | $-21.0932520$ | $-21.0933298$ |
| $N^{14}$ | 0.3919 | $-28.9590082$ | |
| $N^{15}$ | 0.36585 | $-28.9590152$ | $-28.9591137$ |
| $O^{16}$ | 0.3431 | $-38.0746055^-$ | |
| $O^{17}$ | 0.3228 | $-38.0746130$ | $-38.0747323$ |
| $O^{18}$ | 0.3049 | $-38.0746196$ | |
| $F^{19}$ | 0.2888 | $-48.4401009$ | $-48.4402412$ |
| $Ne^{20}$ | 0.2745 | $-60.0555039$ | |
| $Ne^{21}$ | 0.2614 | $-60.0555120$ | $-60.0556735^-$ |
| $Ne^{22}$ | 0.2495 | $-60.0555194$ | |

[a] Reduced atomic energy units are in units of $\mu e^4\hbar^{-2}$. Let $m$ be the mass of the electron and $M$ be the mass of the nucleus, then the reduced mass, $\mu=mM/(M+m)$. For the infinite-mass systems $\mu=m$, and the rydberg is the familiar infinite-mass rydberg.

[14] At first, it might seem more reasonable to optimize for the real, physical systems, and use the thus obtained values for the artificial, infinite-nuclear-mass systems. However, the infinite-nuclear-mass systems serve as a sort of surveyor's bench mark on which everyone can base his work for comparison. Aside from being independent of future improvement of the experimental mass determinations, the choice of the infinite-mass systems also begs the issue of which nuclear isotope to consider.

TABLE II. Isotope shifts.

| System | Rydbergs | Shift $(cm^{-1})$[a] |
|---|---|---|
| $He^3$ | 109717.345 | $1.673\pm0.005$ |
| $He^4$ | 109722.267 | |
| $Li^6$ | 109727.295 | $2.127\pm0.006$ |
| $Li^7$ | 109728.723 | |
| $B^{10}$ | 109731.296 | $3.41\ \pm0.05$ |
| $B^{11}$ | 109731.840 | |
| $C^{12}$ | 109732.291 | $3.82\ \pm0.06$ |
| $C^{13}$ | 109732.678 | |
| $N^{14}$ | 109733.009 | $4.08\ \pm0.06$ |
| $N^{15}$ | 109733.294 | |
| $O^{17}$ | 109733.767 | $4.36\ \pm0.07$ |
| $O^{16}$ | 109733.544 | $8.19\ \pm0.07$ |
| $O^{18}$ | 109733.963 | |
| $Ne^{21}$ | 109734.441 | $4.66\ \pm0.08$ |
| $Ne^{20}$ | 109734.297 | $8.90\ \pm0.08$ |
| $Ne^{22}$ | 109734.571 | |
| $\infty$ | 109737.309 | |

[a] The error estimate is based on the assumption that the pertinent entries in Table I and the rydbergs listed in this table may each be in error by so much as one unit in its last recorded digit.

ordinary secular equation procedure.) The reliability of retaining the infinite mass nonlinear parameter values was checked for all the true mass calculations by varying the nonlinear parameters slightly.[15] The value of the lowest energy found for each value of $Z$ is displayed in Table I for both the infinite-mass calculations and for the more common or stable isotopes of the atoms with nuclear charges from $Z=2$ to 10. Scherr and Machacek found[9] for the three-body systems they studied (two particles identical) that when the charges were all equal in magnitude no stable symmetric state ($^1P$) existed for any mass ratio. Thus, $H^-$ has no stable $^1P$ state. The isotope shift effect[5] data as well as the appropriate Rydberg values used in their evaluation are also entered in Table II.

The differencing technique to recover the perturbation expansion coefficients implicit in the expectation

TABLE III. The $\epsilon_n$ in atomic units.

| $n$ | Recovered here[a] | Knight and Scherr |
|---|---|---|
| 2 | $-0.157023$ | $-0.15702123$[b] |
| 3 | $0.02606$ | $0.02612431$[b] |
| 4 | $0.0061$ | $0.00604561$[c] |
| 5 | $-0.006_1$ | $-0.00442904$[c] |
| 6 | $-0.006$ | $-0.00477658$[c] |

[a] The $Z=2$ value not included in the analysis. The last digit reported is to be regarded as unreliable.
[b] Data from Ref. 10.
[c] Data from Ref. 11, not to be regarded as definitive values.

[15] For the choice of nonlinear parameters $[a,b]$, four additional points $[a,b(1\pm\Delta)]$ and $[a(1\pm\Delta),b]$ were computed, where the $\Delta$'s were some value between 0.001 and 0.00025; except for the He and $Li^+$ systems, of the five points computed the central set, i.e., the values $[a,b]$, was the deepest also in the true mass calculations.

TABLE IV. Recovery of $\langle\Omega\rangle_0$ and $\langle\Omega\rangle_1$.

| Operator | $u^{-1}$ | $u$ | $u^2$ | $r^{-1}$ | $r$ | $r^2$ |
|---|---|---|---|---|---|---|
| Recovered[a] $\langle\Omega\rangle_0$ | 0.25986 | 5.107 | 31.76 | 0.62503 | 3.250⁻ | 16.44 |
| Exact $\langle\Omega\rangle_0$ | 0.259869$\cdots$ | 5.1082$\cdots$ | 31.890$\cdots$ | 0.625 | 3.25 | 16.5 |
| Recovered[a] $\langle\Omega\rangle_1$ | −0.31419 | 5.661 | 71.84 | −0.13069 | 2.721 | 34.29 |
| Knight and Scherr[b] $\langle\Omega\rangle_1$ | −0.314042 | 5.5945 | 67.939 | −0.129932 | 2.6939 | 32.339 |
| Relative error of the recovered $\langle\Omega\rangle_0$ | −0.000042 | −0.00026 | − 0.0040 | 0.000042 | −0.00011 | −0.0038 |
| Relative error[c] of the recovered $\langle\Omega\rangle_1$ | 0.00047[d] | 0.0118 | 0.057 | 0.0058 | 0.0102 | 0.060 |

[a] The $Z=2$ and 3 values are not included in the analysis. In general the last two digits are shaky.
[b] Truncated (i.e., not rounded) from the data of Table III of Ref. 10.
[c] That is, under the assumption that the Knight and Scherr results are the correct values.
[d] Cf. footnote 19.

values was first applied to $E_2(Z)$, defined by

$$E_2(Z) = E(Z) + (5/8)Z^2 - (1705/6561)Z,$$

for $Z$ from 3 to 10 inclusive. The root-mean-square (rms) error estimates for the first few coefficients recovered were judged to be as good as could be expected, and no further refinements were tried. The results are shown in Table III. The differencing technique was also applied directly to the total expectation values of the moments of the interparticle ordinates.

### III. DISCUSSION

#### A. Nonlinear Parameters

Variation of nonlinear parameters is a vexatious procedure, not only because of its time consuming nature, but also because of the nature of the energy surfaces that are developed. Multiple minima abound, and relatively sudden variations, particularly near a minimum, occur. The task in the present instance was somewhat simplified because of the features common to all the surfaces studied. However, as systems of higher and higher $Z$ were studied, the smooth trend of behavior of the parameters was interrupted due to the growth of former secondary minima to the status of true minima. In fact it is possible that the absolute minimum for one or another of the atoms has actually been missed, but it is felt that the energies reported here, if they are indeed not the absolute minima themselves, could not differ from the absolute minima by so much as 5 in the eighth significant figure. Since the reported energies probably differ from the exact eigenvalue in the sixth or seventh decimal place, this is satisfactory minimization.

#### B. Comparison with Pekeris, Schiff, and Lifson

Pekeris, Schiff, and Lifson[2] employed a 220-term variational wave function in a study of the $2P$ and $3P$ states of the helium atom. Their energy result[16] for the

[16] Pekeris, Schiff, and Lifson also present "extrapolated" results which should be very accurate. These are, for the $2\,^1P$ state, −2.1238429 a.u., and for the $3\,^1P$ state, −2.0551460₅ a.u.

(infinite mass) helium $2\,^1P$ state is −2.1238414 a.u. (atomic units). The deeper energy of the 50-term wave function is to be attributed entirely to the fact that Pekeris, Schiff, and Lifson preselected their nonlinear parameters. It was not possible to use their parameter values in the 50-term wave function, as they lie in a region of parameter space inaccessible to the computer program as written. The extrapolation for infinite $Z$ of the optimized parameters found for the 50-term wave functions is not clearcut because of the facts noted in Part A of this section; they extrapolate approximately to $1.005Z$ and $0.64Z$, and the Pekeris, Schiff, and Lifson values to $Z$ and $0.5Z$, correspondingly. As those authors point out, the latter value, $0.5Z$, is necessary to ensure correct behavior at large distances.

An observation that may have bearing on the construction of excited state wave functions concerns the quantitative inferiority of the $3\,^1P$ level obtained in this note compared to the 220-term value. This latter is −2.0551375 a.u., and the 50-term value is −2.0537433 a.u.

#### C. Recovery of Perturbation Energy Coefficients

The Scherr and Silverman analysis[13] of the Pekeris extrapolated results[17] for the ground-state energy values of the helium isoelectronic series later received an unexpected substantiation via a comparison with directly computed higher order coefficients. Seven decimal places of $\epsilon_2$ and six of $\epsilon_3$ were shown to have been obtained correctly by their differencing procedure. The $\epsilon_4$, $\epsilon_5$, and $\epsilon_6$ values had disagreements in the sixth, fifth, and fifth decimal places, respectively. If analogous results can be expected for the recovered $\epsilon_i$ of the present note, then the $\epsilon_5$ and $\epsilon_6$ values are to be expected to be shaky in the third decimal place. Thus, only a qualitative agreement is established between the two sets of data in Table III.

#### D. Recovery of the $\langle\Omega\rangle_n$

Since the $\langle\Omega\rangle_0$ values for all the operators considered are known, these were removed from the data before

[17] C. L. Pekeris, Phys. Rev. 112, 1649 (1958); 115, 1216 (1959).

instituting the differencing analysis. However, as a check, and as a means of getting the "feel" of the data, the raw data were also analyzed. As a general result, the best agreement with the exact $\langle\Omega\rangle_0$ and with the $\langle\Omega\rangle_1$ of Knight and Scherr was obtained when the $Z$ equals 2 and 3 results were not included[18] in the differencing process, and the tabulated results are accordingly based on the $Z$ equals 4 through 10 values only. The results are shown in Table IV (recovery of $\langle\Omega\rangle_0$ and $\langle\Omega\rangle_1$) and Table V (recovery of the higher coefficients after removal of the exact $\langle\Omega\rangle_0$). In the tables, $r$ is the electron-nucleus separation and $u$ is the electron-electron separation. It is comforting to note that in every case but one,[19] after removal of the exact $\langle\Omega\rangle_0$, the recovered $\langle\Omega\rangle_1$ are in closer agreement with the $\langle\Omega\rangle_1$ values of Knight and Scherr than the $\langle\Omega\rangle_1$ entries of Table IV. The associated rms deviations either remained essentially the same or improved slightly.

The variational procedure tinkers most effectively with an approximate wave function in the "energy" region of configuration space, that is, at interparticle distances of the order of 1 a.u. These distances are more important for evaluating operators of the form $r^{-1}$ than, say, $r^2$. These latter depend more sensitively on the description at larger separations. This consideration accounts easily for the much superior recovery of perturbation coefficients from the $\langle u^{-1}\rangle$ and $\langle r^{-1}\rangle$ data than from the other $\langle\Omega\rangle$. This superiority may be seen at a glance from the relative error entries in Table IV. These same data also show that the ease of recovery from the $\langle u\rangle$ is about the same as from the $\langle r\rangle$, and from the $\langle u^2\rangle$ about the same as from the $\langle r^2\rangle$.

### E. Isotope Shifts

The isotope shifts for $Z$ equals 2 and 3 calculated in this note have already been discussed elsewhere.[5,9] The results for the isoelectronic series, presented in Table II, can be roughly fitted to an expression whose leading terms are

$$\text{shift}(\text{cm}^{-1}) = 4.37 \times 10^4 Z^2 m\mu^{-1}(1 - 1.85Z^{-1} + \cdots),$$

where $\mu$ is the magnitude of the difference of the reciprocal masses of the two nuclei involved and $m$ is the electronic mass. If the shift is calculated from a simple, properly symmetrized, product wave function of the type considered by Hughes and Eckart,[4] but using the Pekeris et al.[2] prescription for the orbital exponents, then the result is

$$\text{shift}(\text{cm}^{-1}) = 4.45 \times 10^4 Z^2 m\mu^{-1}(1 - 2.21Z^{-1} + \cdots).$$

Similar calculations have been started for the $^3P$ states of the helium isoelectronic series.

### ACKNOWLEDGMENTS

TABLE V. Recovery[a] of the $\langle\Omega\rangle_n$.

| $\Omega$ | $\langle\Omega\rangle_0$ | $\langle\Omega\rangle_1$ | $\langle\Omega\rangle_2$ |
|---|---|---|---|
| $r^{-1}$ | 5/8 | $-$ 0.13032 | 0.0047 |
| $r$ | 13/4 | 2.714 | 2.300 |
| $r^2$ | 33/2 | 32.96 | 37.3 |
| $u^{-1}$ | 1705/6561 | $-$ 0.31434 | 0.0829 |
| $u$ | 67031/13122 | 5.633 | 4.41 |
| $u^2$ | 1883081/59049 | 69.2 | 75.2 |

[a] The $Z = 2$ and $Z = 3$ values were not included in the analysis of the data. In general the last two digits are shaky.

[18] The result is to be expected occasionally and is a consequence of the nature of the differencing technique. If time permits it is planned to return to this problem.

[19] The somewhat anomalous results obtained with $\langle u^{-1}\rangle_1$ are presumably referrable to the fact that $\langle u^{-1}\rangle_1 = 2\epsilon_2$.