Some calculations on the ground and lowest-triplet state of the helium isoelectronic sequence with the nucleus in motion

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The method described in the preceding paper for the solution of two-electron atoms, which was used to calculate the $1\,^1S$ and $2\,^3S$ states of helium and heliumlike atoms within the fixed-nucleus approximation, has been applied to the case where all three particles are in relative motion. The solutions in the present case automatically include the effects of the mass-polarization term and are compared with the results obtained for the term by using first-order perturbation theory with the fixed-nucleus wave functions. The input data for a particular atom consist of the atomic number, as before, but now the corresponding mass of the nucleus must be given also. Nonrelativistic energies with the nuclear mass included in the calculation have been obtained for the $1\,^1S$ and $2\,^3S$ states for Z ranging from 1 to 10. The energy with the nucleus in motion can be expressed only to eight significant figures (SF's) given the accuracy with which the relevant physical constants are known at present. All the results given here are computed as if these constants were known to ten SF's so that errors are not incurred due to rounding. Convergence of the energies to ten SF's for both the singlet and triplet state was reached with a matrix of size 444 for Z values from 2 to 10. Convergence for the H^- ion was a little slower.

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I. INTRODUCTION

Recently in [1] (this paper will be referred to as I from now on) the authors showed how the body-fixed two-electron Schrödinger equation in generalized perimetric coordinates could be obtained from the laboratory-fixed form of the Schrödinger equation describing a system of three particles. They solved the infinite-nuclear-mass problem in which one of the particles (the heavy nucleus) was considered to be fixed in space and so $m_3 \to \infty$. This simplifies the problem as some of the reduced masses are eliminated. It also makes the only unknown mass in the problem that of the electron. This means that it is possible to work in atomic units (in which the mass of the electron is taken as unity) and to express all the calculated quantities in these units. The precision of these calculated quantities is limited only by the precision of the computational process. The calculated results may then be turned into a form suitable for comparison with experiment by multiplying with an appropriate factor determined in terms of the currently best available physical constant values. The precision of the final results is then limited by the precision with which the constants can be measured, assuming that the computations have been carried out to arbitrary precision.

However, from the form of the body-fixed Hamiltonian given in I, it is clear that there are few extra difficulties in computing the full problem without fixing the nucleus and indeed, only a small amount of extra computer CPU time is needed beyond that for fixed-nucleus calculations. But the problem of precision becomes more vexed. It is

seen from the Hamiltonian form that there is no way of factoring the nuclear masses out of the problem and that the results of a calculation do not scale in any easy way with changes in nuclear mass. It is thus not possible to do each calculation in a set of "atomic units" and to determine the units for comparison with experiment only at the end of the calculation. It is necessary to include the nuclear mass from the beginning in each calculation and that is known only to a particular precision. Any redetermination of its value or change in the precision with which it is known means that the whole calculation must be repeated with the new value and/or to the new precision. The results of such calculations are, therefore, provisional on the values of the physical constants in a rather more intimate way than are the results of clamped nucleus calculations. However, using a computer algebra system (MAPLE) produces expressions for the matrix elements in which both the nuclear charge and the nuclear mass are retained as symbols and so are *not* dependent on their numeric value. Therefore only the program which resolves the symbols into their numeric values need be rerun when data to greater precision become available.

Frost *et al.* [2] were the first to demonstrate how mass effects can be included automatically in the Hamiltonian for a two-electron ion. They generalized the series solution of Pekeris [3] and expanded their wave function in a power series. They then used similarity transformations to take their power series basis into a Laguerre basis so as to obtain symmetric matrices. They used the H^- ion as their subject and showed that for a 50×50 matrix the energy difference due to nuclear mass agreed closely

<u>49</u>   4533

with the value obtained by perturbation theory from the Pekeris fixed-nucleus calculation.

A more recent study of the effects of the nucleus in motion was by Haftel and Mandelzweig [4] who used hyperspherical coordinates separating off the center-of-mass motion. They carried out precise nonvariational calculations of the ground state and $2\,^1S$ state of helium within the infinite-nuclear-mass approximation and in the case of the ground state, with finite nuclear mass too.

Drake [5,6] performed high precision variational calculations on the helium atom and the hydride ion within the fixed-nucleus approximation and was the first to point out the necessity of including mass polarization beyond first-order perturbation theory. Baker et al., p. 123 [7], and Drake, p. 146 [7], both present results for the helium atom to a precision of better than $10^{-4}\,\mathrm{cm}^{-1}$, and conclude that at that level of accuracy, it is *essential* to include the mass-polarization correction in first- and second-order perturbation theory and say that the easiest way to do this is to include the mass-polarization operator in the unperturbed Hamiltonian.

In this work we shall calculate mass-polarization effects to a precision determined only by a knowledge of the physical constants for all the two-electron ions for Z from 1 to 10 in their ground state and for Z from 2 to 10 in their first excited triplet state.

II. METHOD OF SOLUTION

The kinetic energy operator in generalized perimetric coordinates introduced in I is used. For the case of three particles in motion the reduced masses become

$$
\begin{aligned}
\frac{1}{\mu_1} &= \frac{1}{m_1} + \frac{1}{m_3}, & \frac{1}{\mu_2} &= \frac{1}{m_2} + \frac{1}{m_3}, \\
\frac{1}{\mu_3} &= \frac{1}{m_1} + \frac{1}{m_2}, & \frac{1}{\mu_{12}} &= \frac{1}{m_3}, \\
\frac{1}{\mu_{13}} &= \frac{1}{m_1}, & \frac{1}{\mu_{23}} &= \frac{1}{m_2}.
\end{aligned} \tag{1}
$$

Working in atomic units $m_1 = m_2 = 1$ are the electronic masses, and $m_3 = M$, the mass of the nucleus. Using exactly the same approach as in I, the relation

$$
E = -K\epsilon^2, \tag{2}
$$

where K is a nonlinear variation parameter, is used to remove the electronic energy E. Pekeris's [3] forms of the perimetric coordinates which are appropriate for an atom are defined as

$$
u = \epsilon(r_2 + r_3 - r_1), \qquad v = \epsilon(r_1 + r_3 - r_2),
$$
$$
w = 2\epsilon(r_1 + r_2 - r_3), \tag{3}
$$

and are related to those of the kinetic energy (KE) operator Eq. (23) in I by

$$
z_1 = \frac{u}{\epsilon}, \qquad z_2 = \frac{v}{\epsilon}, \quad \text{and} \quad z_3 = \frac{w}{2\epsilon}. \tag{4}
$$

The wave function takes the form

$$
\Psi = e^{-\frac{1}{2}(u+v+w)} F(u,v,w), \tag{5}
$$

which is in principle an exact form as the exponential term contains the correct asymptotic behavior of the solution of the Schrödinger equation. Using the KE operator Eq. (23) in I, the reduced masses of Eq. (1) for the case of finite nuclear mass, and scaling the perimetrics as in Eq. (4) above, the Schrödinger equation $(\hat{H} - E)\Psi = 0$ becomes (after dividing out the asymptotic factor and multiplying by the Jacobian, then dividing by ϵ)

$$
Q + (P + P'/M + KS)\epsilon = 0. \tag{6}
$$

Here,

$$
\begin{aligned}
P ={}& 4uv(u+v+w)(F_{uu} - F_u + F_{vv} - F_v) + 2uw(2u+w)(F_{uu} - F_w + 2F_{ww} - 2F_{uw}) \\
&+ 2vw(2v+w)(F_{vv} - F_w + 2F_{ww} - 2F_{vw}) - 4(u^2 - v^2)(F_u - F_v) + 2(2u+w)(2v+w)(F_u + F_v - 2F_w) \\
&+ 4(u+v)(u+v+w)(2F_w - F) + (1/2)(u+v)(2u+w)(2v+w)F, \\
P' ={}& 4uv(u+v)(F_{uu} + F_{vv} - 2F_{uv})w(u+v)(2u+2v+w)(4F_{ww} - 4F_w + F) \\
&+ 4(v^2 - u^2)(F_u - F_v) + 4(u+v)(u+v+w)(2F_w - F), \\
Q ={}& 4Z(u+v)(u+v+w)F - (2u+w)(2v+w)F, \\
S ={}& -(1/2)(u+v)(2u+w)(2v+w)F,
\end{aligned}
$$

where Z is the nuclear charge, M is the mass of the nucleus, and the subscripts designate partial derivatives. The quantities P and P' arise from the Laplacians, Q from the Coulomb terms, and S from the energy term. It is seen that in Eq. (6) the inverse nuclear mass plays the role of a nonlinear scaling parameter. This observation exemplifies the comments made above about the dependence of the results upon precise values for M.

Just as in I, Eq. (6) is solved by expanding F as

$$
F = \sum_{l,m,n=0}^{\infty} A(l,m,n)\, L_l(u) L_m(v) L_n(w), \tag{7}
$$

where $L_p(x)$ denotes the normalized Laguerre polynomial of order p. The Laguerre recursion relations [see I, Eq. (36)] are used to eliminate all the derivatives and powers of the variables (u,v,w). This leads, just as in I, to a 57-term recursion relation between the coefficients $A(l,m,n)$

in the expansion of the form

$$\sum_{\alpha,\beta,\gamma=-2}^{+2} C_{\alpha,\beta,\gamma}(l,m,n)A(l+\alpha,m+\beta,n+\gamma) = 0. \quad (8)$$

The 57 coefficients in this recursion relation are given in Table I of I for a general case where Z, K, and M are arbitrary.

From this recursion relation a numbering scheme [I, Eq. (42) for singlet states and I, Eq. (43) for triplet states] is used to collapse each triple of indices (l,m,n) to a single index and using the method described in I the infinite secular problem Eq. (8) can be put in the form of a generalized eigenvalue problem

$$\sum_k (F_{ik} - \epsilon G_{ik})B_k = 0, \quad (9)$$

and solved in truncated form of increasing size.

Computational details

The MAPLE computer programs and the C programs written for the fixed-nucleus calculation are readily extended to perform the present calculations. The MAPLE program produces expressions for the matrix elements in which both the nuclear charge and the nuclear mass are retained as symbols. A C program then resolves the symbols into their numeric values on a case-by-case basis. As long as there is sufficient storage for the symbolic forms, this strategy is very efficient.

Table I contains the isotope (the most abundant in each case), and atomic mass, in atomic mass units (amu) and atomic units (a.u.). Z is the atomic number (number of protons) of the nuclide and A is the mass number of the nuclide. The final column contains the mass of the nucleus of the nuclide which is the value used in the work to follow.

The atomic mass is given in unified atomic mass units, $m_u = m_a(^{12}C)/12$. The data were extracted from Wapstra and Audi [8] and are as used in [9], pp. 90 and 91. The value of the unified atomic mass constant m_u is taken to be $1.660\,540\,2(10) \times 10^{-27}$ kg and the mass of an electron m_e to be $9.109\,389\,7(54) \times 10^{-31}$ kg, where

the one-standard-deviation uncertainty in the least significant digits is given in parentheses ([9], p. 81 or [10]). To convert atomic mass units to atomic units the following relationship is used:

$$[M \text{ (a.u.)}] = [M \text{ (amu)}]\frac{m_u}{m_e}.$$

Since m_u and m_e are known only to eight significant figures (SF) at the present time (1988 [10]), the best non-relativistic energy with the nucleus in motion one can obtain is to eight SF's. In Table I the masses (in a.u.) are given ten figures and all the data used in these calculations will be used as if it had ten SF's so that rounding errors are minimized.

III. RESULTS AND DISCUSSION

The scale parameter K was varied to minimize the energy at each order of matrix size, and is shown in row 1 of Table II for the singlet and Table III for the triplet. It was found that K had a dramatic effect on the rate of convergence as found in I for the fixed-nucleus calculation and reached the converged energy (to ten SF's) several iterations before the unscaled energy, equivalent to $K = 1$, did.

For the higher-order matrices the scale parameter K that appeared to minimize the energy was not unique. If K was plotted against the energy, rather than a distinct minimum appearing, the graph would have the form of a flat basin. Therefore, in the tables, if the K value is marked by an asterisk this indicates that a range of values about that value would give that result. For example, the minimizing energy for $Z = 2$ and $n = 252$ was obtained with $K = 1.7$, 1.8, and 1.9. However, in the case where the unscaled $(K = 1)$ energy gave the minimized result, this is the value shown. The reason for this is that, in the limit, the minimized energy should be obtainable without a scale parameter, and this is an indication that the minimized energy has been reached.

The H^- ion $(Z = 1)$ does not appear in Table III as it only has one bound state, which is the singlet state. This was proved rigorously by Nyden Hill within the fixed (infinite-mass) approximation [11] and for the case where the nuclear mass is finite [12].

TABLE I. Atomic data for Z from 1 to 10.

Z	Symbol	A	Mass of atom (amu)	Mass of atom (a.u.)	Mass of nucleus (a.u.)
1	H	1	1.007 825 035	1837.152696	1836.152696
2	He	4	4.002 603 24	7296.299537	7294.299537
3	Li	7	7.016 003 0	12789.39139	12786.39139
4	Be	9	9.012 182 2	16428.20356	16424.20356
5	B	11	11.009 305 4	20068.73654	20063.73654
6	C	12	12 (by definition)	21874.66236	21868.66236
7	N	14	14.003 074 002	25526.04298	25519.04298
8	O	16	15.994 914 63	29156.94642	29148.94642
9	F	19	18.998 403 22	34631.97132	34622.97132
10	Ne	20	19.992 435 6	36443.98154	36433.98154

HAZEL COX, STEPHEN J. SMITH, AND BRIAN T. SUTCLIFFE

TABLE II. The minimizing scale parameter K with superscript asterisk signifying that this value is not unique, the energy parameter ϵ, the energy $-K\epsilon^2$ (in hartrees), and various expectation values for the virial theorem. ϵ is in units of (hartrees)$^{\frac{1}{2}}$ and the expectation values are also in these units. U is the electron-nucleus cusp value and T is the electron-electron cusp value as described in I. The three subrows in each row correspond to matrix sizes of order 252, 444, and 715. This is for the $1\,^1S$ state with nucleus in motion.

Z	1	2	3	4	5	6	7	8	9	10
K	0.8	0.4	0.4	0.4	0.4	0.4	0.4	0.4*	0.4*	0.4*
	0.7	0.3*	0.3	0.3*	0.3*	0.3*	0.3*	0.3*	0.3*	0.3*
	0.6	0.3*	0.3*	0.3*	0.3*	0.3*	0.3*	0.3*	0.3*	0.3*
$-\epsilon$	0.8119774081	2.694116068	4.265946998	5.842668326	7.421227332	9.000657405	10.58060234	12.16085247	13.74131540	15.32189575
	0.8680403845	3.110897275	4.925891297	6.746532262	8.569295196	10.39306395	12.21742722	14.04214289	15.86710429	17.69220127
	0.9375907782	3.110897276	4.925891297	6.746532262	8.569295196	10.39306395	12.21742722	14.04214289	15.86710429	17.69220127
$K\epsilon^2$	0.5274458491	2.903304555	7.279321517	13.654709266	22.029846046	32.40473348	44.77965835	59.15453312	75.52949958	93.90419574
	0.5274458764	2.903304557	7.279321520	13.654709268	22.029846049	32.40473349	44.77965835	59.15453312	75.52949958	93.90419575
	0.5274458804	2.903304558	7.279321520	13.654709268	22.029846049	32.40473349	44.77965835	59.15453312	75.52949958	93.90419575
$-\langle \hat{V} \rangle$	1.623954997	5.388232121	8.531893985	11.68533664	14.84245466	18.00131480	21.16120467	24.32170494	27.48263080	30.64379150
	1.736080796	6.221794552	9.851782593	13.49306452	17.13859039	20.78612790	24.43485444	28.08428579	31.73420858	35.38440254
	1.875181562	6.221794551	9.851782593	13.49306452	17.13859039	20.78612790	24.43485444	28.08428579	31.73420858	35.38440254
$-\langle \hat{K} \rangle$	-0.8119775892	-2.694116053	-4.265946987	-5.842668317	-7.421227325	-9.000657399	-10.58060233	-12.16085247	-13.74131540	-15.32189575
	-0.8680404119	-3.110897277	-4.925891296	-6.746532261	-8.569295196	-10.39306395	-12.21742722	-14.04214289	-15.86710429	-17.69220127
	-0.9375907837	-3.110897275	-4.925891296	-6.746532262	-8.569295196	-10.39306395	-12.21742722	-14.04214289	-15.86710429	-17.69220127
$-\langle \epsilon \rangle$	0.8119774081	2.694116068	4.265946998	5.842668326	7.421227332	9.000657405	10.58060234	12.16085247	13.74131540	15.32189575
	0.8680403845	3.110897275	4.925891297	6.746532262	8.569295196	10.39306395	12.21742722	14.04214289	15.86710429	17.69220127
	0.9375907782	3.110897276	4.925891297	6.746532262	8.569295196	10.39306395	12.21742722	14.04214289	15.86710429	17.69220127
$-(\langle \hat{V} \rangle + \langle \hat{K} \rangle)$	0.8119774081	2.694116068	4.265946998	5.842668326	7.421227332	9.000657405	10.58060234	12.16085247	13.74131540	15.32189575
	0.8680403845	3.110897275	4.925891297	6.746532262	8.569295196	10.39306395	12.21742722	14.04214289	15.86710429	17.69220127
	0.9375907782	3.110897276	4.925891297	6.746532262	8.569295196	10.39306395	12.21742722	14.04214289	15.86710429	17.69220127
U	0.9718444204	1.9847304845	2.9853205201	3.9857310555	4.9860383559	5.9862663793	6.98648502979	7.9866811257	8.9868772209	9.9870329899
	0.9783885003	1.980656141	2.9871926283	3.9873627166	4.9873049863	5.9871307122	6.98693211687	7.9867037913	8.9864715914	9.9861968148
	0.9831285357	1.9902334219	2.9906956295	3.9909216175	4.9910636969	5.9911418282	6.99122038991	7.9912830893	8.9913502981	9.9913807667
T	0.4550988103	0.4734027433	0.4751189338	0.4758363595	0.4762420818	0.47650360959	0.4766879352	0.4768246236	0.4769308400	0.4770142172
	0.4666635111	0.4828711775	0.4831511246	0.4834597698	0.4836641861	0.48380354626	0.4839043418	0.4839797398	0.4840384239	0.4840839616
	0.4731774675	0.4842687796	0.4851608305	0.4855615797	0.4857929630	0.48594336579	0.4860498141	0.4861288818	0.4861903589	0.4862385525

Rows 4–7 of both Tables II and III show the components of the virial theorem. As can be seen for both the singlet and the triplet states $\langle \hat{K} \rangle$ is in good agreement with the energy parameter ϵ and $\langle \hat{V} \rangle$ is twice that. The virial $\langle \hat{K} \rangle + \langle \hat{V} \rangle$ gives ϵ in all cases for all orders of matrices (where $E = -K\epsilon^2$).

The cusp condition for a particle pair is equal to the product of the two charges and the reduced mass of the two particles [see I, Eq. (48)]. Therefore the theoretical electron-electron cusp value is unchanged from its clamped nucleus value of $1/2$ but the electron-nucleus cusp value becomes $-Z\mu_{12}$. In the nucleus in motion approach it would be expected that the exact solution for the singlet, up to linear terms, could be written, after suitable scaling, as

$$\Phi = 1 - Z \left(\frac{M+1}{M} \right) (r_1 + r_2) + \frac{1}{2} r_{12} + \cdots,$$

where M is the mass of the nucleus as given in Table I. However, the reduced mass for the moving nucleus is very near to the value 1 as in the fixed-nucleus case where $M \to \infty$ and the nuclear cusp is $-Z$.

Representing the expansion of our solution in the form

$$\Psi = 1 - U(r_1 + r_2) + Tr_{12} + \cdots,$$

the values of U and T should approach the values of Z (approximately) and $1/2$, respectively, as the basis set size increases, and are given in rows 8 and 9 of Table II for the wave functions for $Z = 1$ to 10, from the nucleus in motion calculation.

Mass correction

Calculating the energies with the nucleus in motion avoids the need to calculate mass-polarization corrections. However, it is of interest to see whether the difference between the nucleus in motion and the fixed-nucleus energies agree with the corrections calculated by Pekeris from his fixed-nucleus calculations.

Some care must be taken in making the comparisons, however, because of the physical constants involved. In the case of fixed-nucleus calculations it is natural to work with the atomic unit of energy defined in terms of the theoretical energy levels of the hydrogen atom with nucleus fixed. Thus the Hartree is defined as

$$E_h = \frac{me^4}{(4\pi\epsilon_0\hbar)^2} = 2R_\infty, \tag{10}$$

where the Rydberg constant for infinite nuclear mass R_∞, is the preferred energy unit of atomic spectroscopists. The theoretical energy levels of the hydrogen atom with the nucleus in motion are given almost as in Eq. (10) but with the electron mass m replaced by the reduced mass μ. It is natural, therefore, to extend the definition of the Rydberg to cover the so-called finite-mass cases by defining

$$R_M = R_\infty \frac{M}{M+m}, \tag{11}$$

TABLE III. The minimizing scale parameter K with superscript asterisk signifying that this value is not unique, the energy parameter ϵ, the energy $-K\epsilon^2$ (in hartrees), and various expectation values for the virial theorem. ϵ is in units of (hartrees)$^{-\frac{1}{2}}$ and the expectation values are also in these units. The three subrows in each row correspond to matrix sizes of order 125, 252, and 444. This is for the $2\,^3S$ state with nucleus in motion.

Z	2	3	4	5	6	7	8	9	10
K	1.9*	1.8*	1.4*	1.3*	1.3*	1.3*	1.3*	1.3*	1.3*
	1.8*	1.2*	1.0*	1.0*	1.0*	1.0*	1.0*	1.0*	1.0*
	1.4*	1.0*	1.0*	1.0*	1.0*	1.0*	1.0*	1.0*	1.0*
$-\epsilon$	1.069906460	1.684954046	2.576902739	3.366481965	4.059156235	4.752046440	5.445062871	6.138166932	6.831318089
	1.099224522	2.063638843	3.049032445	3.838380009	4.628150188	5.418166571	6.208326875	6.998587092	7.788901008
	1.246403452	2.260603090	3.049032445	3.838380009	4.628150188	5.418166571	6.208326875	6.998587092	7.788901008
$K\epsilon^2$	2.174929685	5.110326249	9.296598814	14.733161070	21.419774140	29.356528973	38.543322568	48.980221264	60.666978891
	2.174930189	5.110326330	9.296598848	14.733161097	21.419774162	29.356528993	38.543322587	48.980221284	60.666978911
	2.174930191	5.110326331	9.296598849	14.733161097	21.419774162	29.356528993	38.543322587	48.980221284	60.666978911
$-\langle \hat{V} \rangle$	2.139813083	3.369907955	5.153805498	6.732963964	8.118312483	9.504092885	10.89012574	12.27633386	13.66263618
	2.198449041	4.127277689	6.098064895	7.676760021	9.256300377	10.83633314	12.41665375	13.99717418	15.57780202
	2.492806904	4.521206180	6.098064889	7.676760019	9.256300376	10.83633314	12.41665375	13.99717418	15.57780202
$-\langle \hat{K} \rangle$	−1.069906623	−1.684953908	−2.576902760	−3.366481998	−4.059156248	−4.752046446	−5.445062873	−6.138166933	−6.831318090
	−1.099224519	−2.063638846	−3.049032451	−3.838380011	−4.628150189	−5.418166572	−6.208326875	−6.998587092	−7.788901008
	−1.246403452	−2.260603090	−3.049032445	−3.838380009	−4.628150188	−5.418166571	−6.208326875	−6.998587092	−7.788901008
$-\langle \epsilon \rangle$	1.069906460	1.684954046	2.576902739	3.366481965	4.059156235	4.752046440	5.445062871	6.138166932	6.831318089
	1.099224522	2.063638843	3.049032445	3.838380009	4.628150188	5.418166571	6.208326875	6.998587092	7.788901008
	1.246403452	2.260603090	3.049032445	3.838380009	4.628150188	5.418166571	6.208326875	6.998587092	7.788901008
$-(\langle \hat{V} \rangle + \langle \hat{K} \rangle)$	1.069906460	1.684954046	2.576902739	3.366481965	4.059156235	4.752046440	5.445062871	6.138166932	6.831318089
	1.099224522	2.063638843	3.049032445	3.838380009	4.628150188	5.418166571	6.208326875	6.998587092	7.788901008
	1.246403452	2.260603090	3.049032445	3.838380009	4.628150188	5.418166571	6.208326875	6.998587092	7.788901008

TABLE IV. Energies (in hartrees) of the unscaled $1\,^1S$ state of the helium atom. w is the order of the polynomial and n the order of the corresponding determinant.

w	n	Fixed nucleus, $-E_F$	Nucleus in motion, $-E_M$	$10^4\Delta E$	10^4(Mass correction)
10	161	2.903724111	2.903304291	4.19820	4.1982576
12	252	2.903724290	2.903304470	4.19820	4.1982565
15	444	2.903724356	2.903304536	4.19820	4.1982563
18	715	2.903724370	2.903304550	4.19820	4.1982563
21	1078	2.903724375	2.903304555	4.19820	4.1982563

where M is the mass of the nucleus. Because the theory of the hydrogen atom is so complete and because such accurate experiments can be performed to determine its spectrum (see, for example, [13]) the quantity R_∞ can be determined as a primary constant and is usually quoted directly in cm^{-1}.

As the most accurate calculations of these mass corrections by Pekeris were carried out on the helium atom, this is a good subject of comparison.

For the purpose of comparison, it is necessary to establish the value Pekeris used for the mass of the helium nucleus and the Rydberg constant for infinite nuclear mass and, unfortunately, neither are quoted in his papers. The reference he gives is [14], and within this reference R_∞ is quoted as $109\,737.309 \pm 0.012\,cm^{-1}$ so this is the value used here for comparison purposes.

The total mass correction appearing in the last column of Table IV is calculated from the Rydberg constant R_M, and the so-called mass-polarization correction ϵ_M, defined in Pekeris' papers. The figures in the preceding column are found as the difference between the fixed- and moving-nucleus Pekeris-type $(K=1)$ calculations. It is seen that the entries in the two columns agree pretty well and, interestingly enough, that the entries in the difference column are constant and independent of basis set size to this degree of accuracy.

Table V contains the energies of the $1\,^1S$ states and Table VI those of the $2\,^3S$ states of the relevant two-electron ions. The tables also contain the ionization energies (IE) which are given using the most up-to-date value that we could find of the Rydberg constant for in-

finite nuclear mass [13], $109\,737.315\,683\,0(31)\,cm^{-1}$ with an uncertainty of 2.9×10^{-11} (one standard deviation). The results for this work are calculated using

$$E_{\rm IE} = \left(2E - \frac{M}{M+m}Z^2\right)R_\infty, \qquad (12)$$

where $E = -K\epsilon^2$, the energy for the two electron system in hartrees and the second term in the parentheses is twice the energy for the one electron hydrogenic ion with a moving nucleus, in the same units. By combining the results of Pekeris's Table V and VI of the first paper [3] and using the new R_∞ value and exact nuclear masses to calculate R_M, the figures in the last column of Table V were obtained. This comparison is crude as, apart from helium, Pekeris calculated his energies using a matrix of dimension only 203 and then extrapolated. However, in the case of helium the result of his very accurate calculation with a matrix of dimension 1078 was used.

For the triplet problem, Pekeris calculated only the triplet state of helium. He obtained a nonrelativistic IE for triplet helium of $38\,452.907\,64\,cm^{-1}$ as compared with the value calculated in this work of $38\,452.907\,96\,cm^{-1}$ which again is in very good agreement. The results for the triplet states of the helium isoelectronic sequence are given in Table VI.

Note added in proof. Drake [7] has pointed out that for the helium atom it is possible to achieve an accuracy of 12 SF's by using the ratio of the electron mass to the

TABLE V. Values for the $1\,^1S$ states of the nonrelativistic energy with the nucleus fixed and with the nucleus in motion. The mass effects ΔE and the theoretical value of the ionization energy (IE) using the energy obtained from the nucleus in motion calculation and the results Pekeris obtained for his nonrelativistic IE.

Z	R_M (cm^{-1})	Nucleus fixed, E_F (a.u.)	Nucleus in motion, E_M (a.u.)	Mass effects $\Delta E = E_F - E_M$	Nonrelativistic IE (cm^{-1})	Pekeris's IE (cm^{-1})
1	109677.5834	0.5277510164	0.5274458809	0.0003051355	6083.406871	6083.389355
2	109722.2735	2.903724377	2.903304558	0.000419819	198312.6037	198312.6007
3	109728.7340	7.279913413	7.279321520	0.000591893	610067.8012	610067.7929
4	109730.6347	13.65556624	13.65470927	0.00085697	1241172.129	1241172.117
5	109731.8465	22.03097158	22.02984605	0.00112553	2091696.178	2091696.168
6	109732.2979	32.40624660	32.40473349	0.00151311	3161654.213	3161654.200
7	109733.0156	44.78144515	44.77965835	0.00178680	4451081.243	4451081.231
8	109733.5511	59.15659512	59.15453312	0.00206200	5959972.080	5959972.075
9	109734.1463	75.53171236	75.52949958	0.00221278	7688343.229	7688343.220
10	109734.3038	93.90680651	93.90419575	0.00261076	9636158.364	9636158.356

TABLE VI. Values for the $2\,^3S$ states of the nonrelativistic energy with the nucleus fixed and with the nucleus in motion. The mass effects ΔE and the theoretical value of the ionization energy.

Z	Nucleus fixed, E_F (a.u.)	Nucleus in motion, E_M (a.u.)	Mass effects $\Delta E = E_F - E_M$	Nonrelativistic IE (cm^{-1})
2	2.175229378	2.174930191	0.000299187	38452.90796
3	5.110727373	5.110326331	0.000401042	134028.3816
4	9.297166590	9.296598849	0.000567741	284677.4509
5	14.73389735	14.73316110	0.00073625	490258.9383
6	21.42075590	21.41977416	0.00098174	750734.3135
7	29.35768174	29.35652899	0.00115275	1066095.612
8	38.54464732	38.54332259	0.00132473	1436334.246
9	48.98163833	48.98022128	0.00141705	1861450.161
10	60.66864658	60.66697891	0.00166767	2341432.451

α-particle mass, which is known much more accurately than m_u and m_e.

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