PHYSICAL REVIEW A
GENERAL PHYSICS

THIRD SERIES, VOLUME 34, NUMBER 6 DECEMBER 1986

Specific mass shift for the ^2S ground state of the lithium atom

Frederick W. King
Department of Chemistry, University of Wisconsin—Eau Claire, Eau Claire, Wisconsin 54701
(Received 24 June 1986)

The absolute specific mass shifts for the ^2S ground state of the lithium atom are calculated using a 352-term Hylleraas-type wave function. The specific mass shifts for ^{7}Li and ^{6}Li are 5.180 and 6.042 cm^{-1}, respectively, using first-order perturbation theory, and 5.177 cm^{-1} (^{7}Li) and 6.039 cm^{-1} (^{6}Li) from a nonperturbative approach. With use of Pekeris's accurate values for the specific mass shifts of Li$^+$, the transition isotope shift of Li relative to Li$^+$ is calculated to be 1.101 GHz, using first-order perturbation theory, and 1.071 GHz from a nonperturbative procedure. The calculated shift is in very close agreement with the experimental value of 1.111 ± 0.006 GHz obtained by Lorenzen and Niemax.

I. INTRODUCTION

There has been renewed interest in the determination of specific mass shifts over the last few years.[1,2] The increasing availability of accurate experimental isotope shifts has attracted recent theoretical attention to the calculation of these shifts.[3–5] Because the specific mass shift is rather sensitive to electron correlation effects, there are relatively few calculations of very high quality available in the literature for this quantity. The notable exceptions being the work of Pekeris and co-workers on the ground and excited states of helium and members of its isoelectronic series.[6–12]

The present study was undertaken with two goals in mind. The first was the accurate calculation of the transition isotope shift, using a Hylleraas-type wave function recently determined by King and Shoup.[13] Since this wave function yields approximately 99.97% of the correlation energy, it should be especially suited to the calculation of this correlation-sensitive property. Some observations on the rate of convergence of the expectation value of the specific mass shift and its sensitivity to electron correlation are made. The second objective is that the present calculation forms one step in the sequence of an accurate *ab initio* calculation of the ionization potential of the lithium atom. Assessment of the accuracy of any *ab initio* calculation of state energies involves a comparison with appropriate ionization energies. There are four components of the *ab initio* calculation; the nonrelativistic energy, nuclear mass adjustments which include the normal mass shift and the specific mass shift (mass polarization correction), relativistic corrections, and the Lamb shift. A principle problem of the *ab initio* calculation is the difficulty associated with assessing the accuracy of these individual components, primarily because no direct comparison with experimental values is possible. This is true for the relativistic contribution and for the nonrelativistic ground-state energy. The accuracy of the latter can certainly be assessed by lower-bound techniques, but this is a very difficult computational problem and most often, intractable. There is lacking in the literature experimental data for the quantum electrodynamic shift for states for systems with more than two electrons. The only one of the four contributions for which some independent assessment of the accuracy is possible is the specific mass shift term, particularly for light atoms, where the field shift and relativistic terms involving the nuclear mass (the Stone Hamiltonian[14,15]) are expected to play a fairly minor role.

Considerable progress on the computation of specific mass shifts has been made over the past couple of years by theorists using configuration interaction (CI) methods and many-body techniques.[3–5] The results have been quite impressive, particularly for some of the many-electron systems considered. The present calculation should provide a useful benchmark for such procedures, where the computational errors are typically a few percent or more. Highly accurate calculations of the specific mass shift also offer the potential to assess indirectly the combined importance of relativistic and field shift contributions to the experimental isotope shift. When one or the other of these effects is negligible, the possibility exists to obtain an important check on the Stone formulation of the relativistic contribution, or to gain information on nuclear structure. Such a line of attack has been carried out for the helium atom.[16]

©1986 The American Physical Society

II. THEORY

The effect of finite nuclear mass on the energy levels of an N-electron atomic system is well known[2,17,18] and only a brief outline will be given. The nuclear mass can be accounted for by the addition of the following term to the infinite nuclear mass Hamiltonian:

$$H_{\mathrm{MS}}=\frac{1}{2M}\left[\sum_{i=1}^{N}\mathbf{p}_i\right]^2 , \tag{1}$$

where M is the nuclear mass and $\mathbf{p}_i$ the electronic momentum of the ith electron. H_{MS} separates into two parts, a normal mass shift (also termed the Bohr shift) H_{NMS}, and a specific mass shift H_{SMS} (sometimes referred to as the Hughes-Eckart term);

$$H_{\mathrm{MS}}=H_{\mathrm{NMS}}+H_{\mathrm{SMS}} , \tag{2}$$

where

$$H_{\mathrm{NMS}}=\frac{1}{2M}\sum_{i=1}^{N}p_i^2 \tag{3}$$

and

$$H_{\mathrm{SMS}}=\frac{1}{M}\sum_{i=1}^{N}\sum_{j>i}^{N}\mathbf{p}_i\cdot\mathbf{p}_j . \tag{4}$$

The shift of the energy levels due to the normal mass effect is handled in a straightforward manner by the introduction of a reduced-mass Rydberg constant R_M, so that the shifted levels are $R_M E_\infty$, where E_∞ signifies the energy of the level of interest in the infinite nuclear mass model. The specific mass shift is far more difficult to handle in comparison with the normal mass shift. As indicated above, the specific mass shift is very sensitive to electron correlation effects. For the lithium atom ground state treated in the Hartree-Fock approximation, the expectation value of H_{SMS} is zero, and it is therefore essential to evaluate the specific mass shift using a wave function which adequately accounts for electron correlation.

The energy shift due to the specific mass term, ΔE_{SMS}, has been calculated by two procedures in the present work. ΔE_{SMS} has been evaluated by first-order perturbation theory using the wave function determined from the normal Hamiltonian (no specific mass shift operator present). The appropriate expression is

$$\Delta E_{\mathrm{SMS}}=-\frac{\mu}{M}\left\langle\psi\left|\sum_{\substack{i,j\\(i<j)}}\nabla_i\cdot\nabla_j\right|\psi\right\rangle , \tag{5}$$

where μ is the reduced electron mass. The appearance of m_e (the electron mass) in the denominator of μ/M is often omitted; its impact on the value of ΔE_{SMS} is below the current uncertainty in the experimental measurements. ΔE_{SMS} has also been determined by including H_{SMS} with the rest of the Hamiltonian and solving

$$\left[-\frac{1}{2\mu}\sum_{i=1}^{3}\nabla_i^2-\frac{1}{M}\sum_{i=1}^{3}\sum_{j>i}^{3}\nabla_i\cdot\nabla_j+V\right]\psi=E\psi , \tag{6}$$

from which ΔE_{SMS} has been evaluated as the expectation of H_{SMS}, Eq. (4), using the eigenfunction obtained from Eq. (6). In Eq. (6), V is the appropriate potential operator for the lithium atom. An alternative operator form for ΔE_{SMS} has been given by Vinti,[19] but this has received far less attention in the literature.[20]

The calculations reported in this work were carried out using a 352-term Hylleraas-type wave function of the form

$$\psi=\mathscr{A}\sum_{\mu=1}^{352}C_\mu\phi_\mu\chi_\mu , \tag{7}$$

where $\mathscr{A}$ is the antisymmetrizer and C_μ are the variationally determined expansion coefficients. The basis functions ϕ_μ are of the form

$$\begin{aligned}&\phi_\mu(r_1,r_2,r_3,u_1,u_2,u_3)\\&\quad\equiv\phi_\mu(i,j,k,l,m,n,\alpha,\beta,\gamma)\\&\quad=r_1^{i_\mu}r_2^{j_\mu}r_3^{k_\mu}u_1^{l_\mu}u_2^{m_\mu}u_3^{n_\mu}\exp(-\alpha_\mu r_1-\beta_\mu r_2-\gamma_\mu r_3)\end{aligned} \tag{8}$$

where $u_1=r_{23}$, $u_2=r_{31}$, and $u_3=r_{12}$, and the exponents i_μ, j_μ, k_μ, l_μ, m_μ, and n_μ are each greater than or equal to 0. In Eq. (7) χ denotes the doublet spin eigenfunctions. There are two such functions:

$$\chi=\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3) \tag{9a}$$

or

$$\chi=2\alpha(1)\alpha(2)\beta(3)-\beta(1)\alpha(2)\alpha(3)-\alpha(1)\beta(2)\alpha(3) . \tag{9b}$$

For a complete description of the details on the basis functions selected in Eq. (7), the reader is referred to Ref. 13.

Since the basis functions given in Eq. (8) depend explicitly on the interelectronic coordinates, considerable simplification of the necessary matrix elements results if H_{SMS} is expressed in terms of the interelectronic coordinates. In these coordinates H_{SMS} takes the form (in a.u.)

$$\begin{aligned}H_{\mathrm{SMS}}&=-\frac{1}{M}\sum_{i=1}^{3}\sum_{j>1}^{3}\nabla_i\cdot\nabla_j\\&=\frac{1}{M}\left\{\sum_{i=1}^{3}\left[\frac{\partial^2}{\partial u_i^2}+\frac{2}{u_i}\frac{\partial}{\partial u_i}\right]\right.\\&\qquad\left.+\sum_{\mathscr{P}_{ijk}}\left[\left[\frac{u_i^2+u_j^2-u_k^2}{4u_iu_j}\right]\frac{\partial^2}{\partial u_i\partial u_j}-\left[\frac{r_i^2+r_j^2-u_k^2}{4r_ir_j}\right]\frac{\partial^2}{\partial r_i\partial r_j}+\left[\frac{r_i^2-r_j^2+u_k^2}{2r_iu_k}\right]\frac{\partial^2}{\partial r_i\partial u_k}\right]\right\} .\end{aligned} \tag{10}$$

TABLE I. Basis functions and coefficients resulting from the action of the operator $\sum_{i,j\,(i<j)} \nabla_i \cdot \nabla_j$ on $\phi(i,j,k,l,m,n,\alpha,\beta,\gamma)$ [see Eq. (11)].

Term	$i'-i$	$j'-j$	$k'-k$	$l'-l$	$m'-m$	$n'-n$	Coefficient[a] $c_{ijklmn}^{i'j'k'l'm'n'}$
1	-1	0	0	0	0	0	$\alpha(m+n-k-j)$
2	0	-1	0	0	0	0	$\beta(l+n-i-k)$
3	0	0	-1	0	0	0	$\gamma(l+m-i-j)$
4	-2	0	0	0	0	0	$i(j+k-m-n)$
5	0	-2	0	0	0	0	$j(i+k-l-n)$
6	0	0	-2	0	0	0	$k(i+j-l-m)$
7	0	0	0	-2	0	0	$-l(2l+2+j+k+m+n)$
8	0	0	0	0	-2	0	$-m(2m+2+i+k+l+n)$
9	0	0	0	0	0	-2	$-n(2n+2+i+j+l+m)$
10	1	0	0	0	-2	0	αm
11	1	0	0	0	0	-2	αn
12	0	1	0	-2	0	0	βl
13	0	1	0	0	0	-2	βn
14	0	0	1	-2	0	0	γl
15	0	0	1	0	-2	0	γm
16	2	-1	0	0	0	-2	$-\beta n$
17	2	0	-1	0	-2	0	$-\gamma m$
18	0	2	-1	-2	0	0	$-\gamma l$
19	-1	2	0	0	0	-2	$-\alpha n$
20	0	-1	2	-2	0	0	$-\beta l$
21	-1	0	2	0	-2	0	$-\alpha m$
22	-2	2	0	0	0	-2	in
23	-2	0	2	0	-2	0	im
24	2	-2	0	0	0	-2	jn
25	0	-2	2	-2	0	0	jl
26	2	0	-2	0	-2	0	km
27	0	2	-2	-2	0	0	kl
28	0	0	0	-2	-2	2	lm
29	0	0	0	-2	2	-2	ln
30	0	0	0	2	-2	-2	mn
31	1	-1	0	0	0	0	$\alpha\beta$
32	1	0	-1	0	0	0	$\alpha\gamma$
33	-1	1	0	0	0	0	$\alpha\beta$
34	0	1	-1	0	0	0	$\beta\gamma$
35	-1	0	1	0	0	0	$\alpha\gamma$
36	0	-1	1	0	0	0	$\beta\gamma$
37	-1	-1	0	0	0	2	$-\alpha\beta$
38	-1	0	-1	0	2	0	$-\alpha\gamma$
39	0	-1	-1	2	0	0	$-\beta\gamma$
40	-2	1	0	0	0	0	$-i\beta$
41	-2	0	1	0	0	0	$-i\gamma$
42	1	-2	0	0	0	0	$-j\alpha$
43	0	-2	1	0	0	0	$-j\gamma$
44	1	0	-2	0	0	0	$-k\alpha$
45	0	1	-2	0	0	0	$-k\beta$
46	-2	-1	0	0	0	2	$i\beta$
47	-2	0	-1	0	2	0	$i\gamma$
48	-1	-2	0	0	0	2	$j\alpha$
49	0	-2	-1	2	0	0	$j\gamma$
50	-1	0	-2	0	2	0	$k\alpha$
51	0	-1	-2	2	0	0	$k\beta$
52	-2	-2	0	0	0	2	$-ij$
53	-2	0	-2	0	2	0	$-ik$
54	0	-2	-2	2	0	0	$-jk$

[a] Each coefficient entry must be multiplied by $\frac{1}{2}$.

In Eq. (10) $\mathscr{P}_{ijk}$ signifies summation over the six permutations $\binom{1\ 2\ 3}{i\ j\ k}$. With the preceding form for H_{SMS}, advantage can be taken of the fact that

$$-MH_{\mathrm{SMS}}\phi(i,j,k,l,m,n,\alpha,\beta,\gamma)$$

$$=\sum_{\substack{s,t\\(s<t)}}^{3}\nabla_s\cdot\nabla_t\phi(i,j,k,l,m,n,\alpha,\beta,\gamma)$$

$$=\sum c_{ijklmn}^{i'j'k'l'm'n'}\phi(i',j',k',l',m',n',\alpha,\beta,\gamma)\ , \quad (11)$$

where the $c_{ijklmn}^{i'j'k'l'm'n'}$ are determined coefficients in the linear algebraic decomposition of the left-hand side of Eq. (11). The decomposition given by Eq. (11) is significant because the expectation value of H_{SMS} can be represented as a sum of overlap integrals of the form

$$I(i,j,k,l,m,n,\alpha,\beta,\gamma)$$

$$=\int r_1^i r_2^j r_3^k u_1^l u_2^m u_3^n e^{-\alpha r_1-\beta r_2-\gamma r_3}d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ . \quad (12)$$

The method used to evaluate these integrals is that of Öhrn and Nordling.[21] The 54 terms generated in Eq. (11) are tabulated in Table I. The I integrals [Eq. (12)] arising from the first group of 30 terms given in Table I are also required in the evaluation of the electron nuclear potential energy and the kinetic energy. A significant reduction in computational effort can be obtained by calculating part of the expectation value of H_{SMS} at the same time the matrix elements of the electron nuclear potential energy and the kinetic energy are evaluated.

III. RESULTS

The results of the calculations are presented in Tables II, III, and IV. The expectation value $\langle \sum_{i,j\,(i<j)}\nabla_i\cdot\nabla_j\rangle$ has been appropriately scaled using the scale factor

$$\eta=\frac{-\frac{1}{2}\langle V\rangle}{\langle T\rangle}\ , \quad (13)$$

where $\langle V\rangle$ and $\langle T\rangle$ are the potential energy and kinetic energy, respectively. For the final value of $\langle \sum_{i,j\,(i<j)}\nabla_i\cdot\nabla_j\rangle$ reported in Table II using the 352-term wave function, the scale factor has the value 1.000001, and clearly this has an almost negligible impact on the calculated expectation value.

In Table III, the value reported for $\langle \sum_{i,j\,(i<j)}\nabla_i\cdot\nabla_j\rangle$ for Martensson and Salomonson was deduced from their reported isotope shift (in GHz) and the value of $\langle\nabla_1\cdot\nabla_2\rangle$ for Li^+ calculated by Pekeris,[8] that is, $-0.288\,994\,0$ a.u. The conversion factor from atomic units to GHz employed is 1 a.u.$\equiv$85.618 41 GHz. This factor corresponds to

$$29.979\,245\,8\left[\frac{{}^{6}\mu}{M_{{}^{6}\mathrm{Li}}}2R_{{}^{6}\mathrm{Li}}-\frac{{}^{7}\mu}{M_{{}^{7}\mathrm{Li}}}2R_{{}^{7}\mathrm{Li}}\right]\ ,$$

where $M_{{}^{6}\mathrm{Li}}$ and $M_{{}^{7}\mathrm{Li}}$ are the nuclear masses for the lithium isotopes 6 and 7, respectively. The values employed are taken from the atomic mass tables of Wapstra and Bos,[24] and have been corrected for the mass of three electrons: $M_{{}^{6}\mathrm{Li}}=6.013\,477\,5\ u$ and $M_{{}^{7}\mathrm{Li}}=7.014\,358\,8\ u$. ${}^{6}\mu$ and ${}^{7}\mu$ denote the reduced mass of the electron for isotopes 6 and 7, respectively. $R_{{}^{6}\mathrm{Li}}$ represents the reduced mass Rydberg constant for isotope 6 and $R_{{}^{7}\mathrm{Li}}$ has a similar meaning for isotope 7. The values employed were calculated from R_∞ (using[25] $R_\infty=109\,737.315\,21\ \mathrm{cm}^{-1}$); $R_{{}^{7}\mathrm{Li}}=109\,728.73\ \mathrm{cm}^{-1}$ and $R_{{}^{6}\mathrm{Li}}=109\,727.31\ \mathrm{cm}^{-1}$.

The value of $\langle \sum_{i,j\,(i<j)}\nabla_i\cdot\nabla_j\rangle$ reported in Table III for Chambaud *et al.* was calculated from their reported absolute shift using their conversion factor 1 a.u.$=$85.647 GHz, which corresponds to replacing μ by m_e and R_M by R_∞ in the conversion factor reported above.

For each of the isotope shifts tabulated in Table IV, except the present calculation, the transition shift has been determined from values calculated for Li and Li^+ in each of the studies reported. The isotope shift calculated in the present study employed the absolute shift for Li^+ determined from Pekeris's accurate calculation,[8] that is, 24.743 18 GHz.

IV. DISCUSSION

A. Convergence characteristics

The convergence of the calculated value of the matrix element $\langle \sum_{i,j\,(i<j)}\nabla_i\cdot\nabla_j\rangle$ as a function of the number of

TABLE II. Expectation values (in a.u.) of the operator $\sum_{i=1}^{3}\sum_{j>i}^{3}\nabla_i\cdot\nabla_j$ as a function of the number of terms in the wave function.

Number of terms	$\left\langle \sum_{\substack{i,j\\(i<j)}}\nabla_i\cdot\nabla_j\right\rangle$	Number of terms[b]	$\left\langle \sum_{\substack{i,j\\(i<j)}}\nabla_i\cdot\nabla_j\right\rangle$
60	−0.312 133	50	−0.303 609
150	−0.302 706	100	−0.302 253
210	−0.302 218	150	−0.301 970
280	−0.301 898	200	−0.301 915
320	−0.301 888	251	−0.301 859
352	−0.301 848		

[a] Both spin functions included.
[b] Only spin function 1 included; Eq. (9a).

TABLE III. Absolute specific mass shifts for the ^2S ground-state levels of ^{6}Li and ^{7}Li. MBPT stands for many-body perturbation theory.

Wave function	Type	Number of terms	$\left\langle \sum_{\substack{i,j \\ (i<j)}} \nabla_i \cdot \nabla_j \right\rangle$ (a.u.)	Absolute specific mass shift (cm^{-1}) ^{7}Li	^{6}Li
Prasad and Stewart[a]	CI	45	−0.3014	5.173	6.033
Martensson and Salomonson[b]	MBPT		−0.3002[e]	5.152	6.009
Chambaud, Lévy, and Stacey[c]	CI		−0.3055[e]	5.243	6.116
Veseth[d]	MBPT		−0.3047	5.2296	6.100
Present work	Hylleraas (single spin eigenfunction)	251	−0.301 86	5.1805	6.0426
Present work	Hylleraas (both doublet spin functions)	352	−0.301 85	5.1803	6.0424

[a]Reference 22.
[b]Reference 3.
[c]Reference 4.
[d]Reference 5.
[e]See the text for comments on the calculation of these values.

terms in the wave function can be gauged from the results presented in Table II. The convergence is not monotone. The nonuniform convergence is tied in part to the procedure employed for the basis set selection. The larger change in the matrix element for the last 32 terms ($\sim 4\times 10^{-5}$ a.u.) compared with the previously added 40 terms ($\sim 1\times 10^{-5}$ a.u.), reflects a superior selection of basis functions that have much greater impact on the energy, and also account for electron correlation in an improved manner. Since $\langle \sum_{i,j\,(i<j)} \nabla_i \cdot \nabla_j \rangle$ is sensitive to electron correlation effects, the change in the value of this matrix element over the last 32 terms directly reflects this fact.

Because of the nonuniform nature of the convergence, it does not appear useful to attempt an extrapolation procedure for $\langle \sum_{i,j\,(i<j)} \nabla_i \cdot \nabla_j \rangle$. A rough estimate of the error in this expectation value is $\sim 5\times 10^{-5}$ a.u. Since the variational approach leads to generally better results for expectation values emphasizing the energy important region of configuration space, the aforementioned estimate of uncertainty should be reasonable. A cautionary note, however, is that the specific mass shift is somewhat more sensitive to electron correlation effects than the matrix elements of the kinetic and potential energy.

TABLE IV. Isotope shifts for the ^2S ground state of the lithium atom. The isotope shift is defined by $(\Delta E_{\mathrm{SMS}}^{^7\mathrm{Li}^+} - \Delta E_{\mathrm{SMS}}^{^7\mathrm{Li}}) - (\Delta E_{\mathrm{SMS}}^{^6\mathrm{Li}^+} - \Delta E_{\mathrm{SMS}}^{^6\mathrm{Li}})$.

Wave function	Shift for ^{6}Li-^{7}Li (GHz)	Shift for ^{6}Li$^+$-^{7}Li$^+$ (GHz)	Isotope shift (GHz)
Prasad and Stewart[a]	25.80_5	24.81_2	0.993
Martensson and Salomonson[b]			0.962
Chambaud, Lévy, and Stacey[c]	26.165	25.077	1.088
Veseth[d]	26.090	25.007	1.083
Present work (single spin eigenfunction)	25.845		1.102
Present work (both spin eigenfunctions)	25.844		1.101
Experimental[e]			1.111±0.006

[a]Reference 22.
[b]Reference 3.
[c]Reference 4.
[d]Reference 5.
[e]Reference 23.

B. Effects of one versus two spin eigenfunctions

From Table II, it is apparent that the value of $\langle \sum_{i,j\,(i<j)} \nabla_i \cdot \nabla_j \rangle$ is changed only by a very minor amount when it is evaluated using a wave function containing only the spin eigenfunction given in Eq. (9a). This behavior is not totally unexpected, and supports the general observation, based on the calculation of a number of different expectation values, that the second doublet spin eigenfunction has a very minor impact on the calculation of a spin-independent property.[13]

C. Comparison with experiment

The principal experimental measurement available for comparison with the calculations of this study, is the work of Lorenzen and Niemax,[23] where the transition isotope shift of the ^2S ground state of Li relative to the ^1S ground state of Li^+ has been measured. The value reported for this transition shift is 1.111±0.006 GHz. The value calculated for this shift in the present work using first-order perturbation theory is 1.101 GHz, with an estimated probable error of ±0.040 GHz. The uncertainty is based on the error estimate given in Sec. IV A.

The results of other accurate calculations of this shift are tabulated in Table IV. The most accurate value reported previously is that of Chambaud *et al.*,[4] who report a value that is approximately 2.1% too low. Unfortunately, their close agreement with the experimental result rests on a cancelation of errors in the difference between the calculated specific mass shifts of the neutral atom and the single positive ion, a fact the authors themselves point out. Their result for the absolute shift of Li^+ is somewhat above the accurate value obtained by Pekeris.[8] If the transition shift of Chambaud *et al.* is recalculated using the more accurate value of Pekeris for Li^+, then the resulting value is 1.422 GHz, which is about 28% too high.

The result reported by Veseth[5] (Table IV) is approximately 2.5% too low. It is to be noted that Veseth's close agreement with the experimental result also rests on a cancelation of errors between the calculated shifts for the neutral atom and positive ion. If Veseth's isotope shift is recalculated using the Pekeris value for Li^+, then the result is 1.347 GHz, about 21% above the experimental result. The purpose of recalculating the transition isotope shifts of Chambaud *et al.* and Veseth (using the Pekeris result for Li^+) has been to provide an estimate of the error cancelation that occurs in their calculations. The present recalculation does highlight the extremely useful feature of their calculations, namely, a quality and consistent basis set description of the $1s$ core for Li and Li^+ is adequate for a very accurate calculation of the transition isotope shift. This advantage is obviously lost when the Pekeris result for Li^+, with its far superior description of the $1s$ core, is employed.

It should be clear from the calculations of Chambaud *et al.* and Veseth, that a very high accuracy is required in the calculation of each individual shift (both neutral atom and ion), since the transition isotope shift corresponds to the difference between two values which are rather close together. For excited states of the lithium atom of S symmetry, the situation is much more demanding, since the isotope shifts are much smaller than for the ground state. There is clearly a challenging theoretical problem to be resolved for these states.

When the entire eigenvalue problem [Eq. (6)] was solved, the results obtained for the expectation value $\langle \sum_{i,j\,(i<j)} \nabla_i \cdot \nabla_j \rangle$ were $-0.301\,660$ a.u. for ^{7}Li and $-0.301\,628$ a.u. for ^{6}Li, and the relative isotope shift was determined to be 1.071 GHz. These values, not surprisingly, are in close agreement with the values presented in Tables II and IV, which are based on first-order perturbation theory.

A possible explanation for the increased discrepancy of the nonperturbative result with the experimental measurement is as follows. The higher-order specific mass shift contributions for Li are not canceled by the expectedly similar contributions left out of the first-order result employed for Li^+. Unfortunately, it is not possible to test this conjecture, since a nonperturbative result with the Pekeris wave function is not available for Li^+. It is also important to keep in mind that the slow convergence of the present calculation leads to an error in the transition isotope shift, which is larger than the changes obtained on going from first-order perturbation theory to the nonperturbative approach.

Two factors have not been incorporated in the present calculation of the transition isotope shift. The first is the field shift contribution. For a light atom such as lithium, this shift is expected to be very small. Veseth[5] has made a recent calculation of the field shift contribution to the isotope shift for lithium and obtains the value −0.0006 GHz.

The second factors not included in the present calculations are the relativistic corrections to the shift. For light atoms, such corrections would be expected to be small. For the lithium atom no relativistic calculations on the isotope shift have been made. However, de Clercq *et al.*[16] have examined relativistic effects for the He atom, and have found relativistic corrections to various transition isotope shifts of approximately 0.01 GHz. It seems not entirely unreasonable that part of the discrepancy between theory and experiment for the Li atom may be accounted for by small relativistic effects.

V. CONCLUSION

The present study has reported the most accurate calculation of an absolute specific mass shift for a system with more than two electrons. The value obtained for the relative isotope shift is in very close agreement with the experimental value. There is, however, a clear need for more accurate calculations in order to reduce the estimated error to approximately 0.001 GHz. If this can be achieved, and the experimental error limits also further reduced, the possibility exists to determine the importance of nuclear mass dependent relativistic corrections to the isotope shifts. This would provide an important test of the Stone Hamiltonian. This proposal rests on the assumption that the field shift is negligibly small for the lithium atom.

ACKNOWLEDGMENTS

The author thanks the University of Wisconsin—Eau Claire computer center for their generous allocation of computer time, which made this project possible. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The author was also supported by funds from the Camille and Henry Dreyfus Foundation.

---

[1] J. Bauche and R.-J. Champeau, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and B. Bederson (Academic, New York, 1976), Vol. 12, p. 39.

[2] W. H. King, *Isotope Shifts in Atomic Spectra* (Plenum, New York, 1984).

[3] A.-M. Martensson and S. Salomonson, J. Phys. B **15**, 2115 (1982).

[4] G. Chambaud, B. Lévy, and D. N. Stacey, J. Phys. B **17**, 4285 (1984).

[5] L. Veseth, J. Phys. B **18**, 3463 (1985).

[6] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[7] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

[8] C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

[9] C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).

[10] C. L. Pekeris, Phys. Rev. **127**, 509 (1962).

[11] B. Shift, H. Lifson, C. L. Pekeris, and P. Rabinowitz, Phys. Rev. **140**, A1104 (1965).

[12] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).

[13] F. W. King and V. Shoup, Phys. Rev. A **33**, 2940 (1986).

[14] A. P. Stone, Proc. Phys. Soc. London **77**, 786 (1961).

[15] A. P. Stone, Proc. Phys. Soc. London **81**, 868 (1963).

[16] E. de Clercq, F. Biraben, E. Giacobino, G. Grynberg, and J. Bauche, J. Phys. B **14**, L183 (1981).

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

[18] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977), p. 166.

[19] J. P. Vinti, Phys. Rev. **58**, 882 (1940).

[20] M. R. Flannery and A. L. Stewart, Proc. Phys. Soc. London **81**, 431 (1963); C. Froese Fischer and L. Smentek-Mielczarek, J. Phys. B **16**, 3479 (1983).

[21] Y. Öhrn and J. Nordling, J. Chem. Phys. **39**, 1864 (1963).

[22] S. S. Prasad and A. L. Stewart, Proc. Phys. Soc. London **87**, 159 (1966).

[23] C.-J. Lorenzen and Niemax, J. Phys. B **15**, L139 (1982).

[24] A. H. Wapstra and K. Bos, At. Data Nucl. Data Tables **19**, 175 (1977).

[25] T. W. Hänsch, in *Advances in Laser Spectroscopy*, edited by F. T. Arecchi, F. Strumia, and H. Walther (Plenum, New York, 1981), Vol. 65, p. 127.