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Isotope Shift in Neutral Carbon*

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There is a possibility that the discrepancy between the experimental values of spectral isotope shift in light elements and the values calculated by including nuclear motion may be reduced by using improved one-electron wave functions. In order to investigate this possibility and at the same time to make a comparison with recently obtained experimental data, the shift of the transition $2p^2\,{}^1S-2p3s\,{}^1P(\lambda=2478.5\text{A})$ of neutral carbon has been calculated using Hartree one-electron functions without exchange. The functions for the $2p3s$ configuration were calculated by the author for this purpose. The agreement with the experimental value is comparable to that obtained for other elements with this type of function. A comparison of the term shifts is made for both the ${}^3P$ and ${}^1S$ terms of the $2p^2$ configuration using Hartree functions with and without exchange and analytic functions of the Morse, Young, and Haurwitz type. The use of functions with exchange produced a significant change in the calculated term shifts which indicates that it may be possible to improve the agreement between calculated and observed transition shifts.

INTRODUCTION

EXPERIMENTAL measurements of the isotope shift of the spectral line $2p^2\,{}^1S_0-2p3s\,{}^1P_1(\lambda=2478.5\text{A})$ in neutral carbon have been reported by two investigators.[1,2] Each reported a value of -0.156 ± 0.002 cm^{-1} for the shift from C^{12} to C^{13} and one[1] reported a value of -0.294 ± 0.002 cm^{-1} for the shift from C^{12} to C^{14}. A method has been published previously[3] for calculating a theoretical value for the difference of energy levels in light atoms due to nuclear motion. Application of the method to lithium,[4] boron,[5] neon,[3] and magnesium[6] has produced varying degrees of agreement with experimentally determined shifts. Before presenting the results obtained by calculating some shifts in neutral carbon, a brief review of the theory will be presented following the notation used by Vinti.[6]

It has been shown by Bartlett and Gibbons,[3] that the assumption of a finite nuclear mass adds a term to the Hamiltonian of an atom equal to

$$(2M)^{-1}\left(\sum_{i=1}^{\nu}\mathbf{p}_i\right)^2,$$

where $\mathbf{p}_i$ is the linear momentum of the ith electron relative to the nucleus and M is the nuclear mass. This term can be expressed as the sum of two terms,

$$N=(2M)^{-1}\sum_{i=1}^{\nu}\mathbf{p}_i^2 \quad\text{and}\quad \sigma=M^{-1}\sum_{i>j}\sum\mathbf{p}_i\cdot\mathbf{p}_j.$$

The quantity N is customarily called the "normal" shift. It can be shown that its effect is to add a term $-(m/M)E$ to the unperturbed eigenfunctions, where E is the observed total energy. This is equivalent to assuming a reduced mass for the electrons as is done in the case of the hydrogen atom. The second term is customarily called the "specific" shift. Its effect cannot be evaluated exactly but since it is small compared to the energy of the atom, first-order perturbation theory can be applied. Russell-Saunders coupling is assumed and the spin-orbit terms in the Hamiltonian are assumed small enough to be neglected.

In order to evaluate the effects of the term σ, it is necessary to obtain the diagonal elements $\bar{\sigma}$ of the corresponding operator with respect to the unperturbed wave functions. It is not necessary to calculate any off-diagonal elements since the Slater diagonal sum rule can be applied. If determinantal wave functions U are formed from an orthogonal set of one-electron functions of the form $R(n,l)(r)f(\theta,\phi)\alpha(s)$, expressions for evaluating the necessary diagonal elements can be derived.[6] These expressions are of the form:

$$(U|\sigma|U)=-M^{-1}\sum_{\mu>\rho}\sum|(n,l,m_l|\times\mathbf{p}|n',l-1,m_l')|^2\delta(m_s,m_s'),$$

where μ and ρ represent the sets of quantum numbers n, l, m_l, m_s, and n', l', m_l', m_s', respectively. The $\delta(m_s,m_s')$ indicates that the spins of the two orbits μ and ρ are the same. The sums are extended over all occupied orbits. The nonzero terms in the double sum can be expressed[6] as:

$$|(n,l,m_l|\mathbf{p}|n',l-1,m_l)|^2=C_l^2(l^2-m_l^2)(2mRy)J^2(n,l;n',l-1),$$

$$|(n,l,m_l|\mathbf{p}|n',l-1,m_l\mp1)|^2=\tfrac{1}{2}C_l^2(l\pm m_l-1)(l\pm m_l)(2mRy)J^2(n,l;n',l-1),$$

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[1] J. R. Holmes, Phys. Rev. **77**, 745 (1950); J. Opt. Soc. Am. **41**, 360 (1951).

[2] C. R. Burnett, Phys. Rev. **80**, 494 (1950).

[3] J. H. Bartlett and J. J. Gibbons, Jr., Phys. Rev. **44**, 538 (1933).

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

[5] W. Opechowski and D. A. DeVries, Physica **6**, 913 (1939); J. P. Vinti, Phys. Rev. **58**, 879 (1940).

[6] J. P. Vinti, Phys. Rev. **56**, 1120 (1939).

where Ry is the Rydberg energy,

$$C_l=[(2l+1)(2l-1)]^{-\frac{1}{2}},$$

and

$$J(n,l;n',l-1)=\int_0^\infty R(nl)\times\left[\frac{dR(n',l-1)}{dr}-\frac{l-1}{r}R(n',l-1)\right]r^2dr.$$

In these integrals the radial parts of the one-electron functions $R(nl)$ are assumed to be so normalized that

$$\int_0^\infty R^2r^2dr=1.$$

The variable of integration r is expressed in units of the Bohr radius and the units of $\bar{\sigma}$ are cm^{-1}.

It is apparent that it is necessary to know the radial parts of the one-electron wave functions $R(nl)$ in order to evaluate the integrals. The sum of the two quantities $\bar{N}$ and $\bar{\sigma}$ mentioned before gives the energy shift from an atom of infinite nuclear mass to one of mass M. In order to calculate the shift between isotopes, it is necessary to calculate the shift from an infinite nuclear mass to each of the two isotopic masses and to take the difference between the two. In order to calculate the frequency shift in a given transition, it is necessary to calculate the shift of each of the energy levels of the transition and take their difference. It can be shown from the properties of the operators N and σ that to the approximation used, all the levels of a given multiplet have the same shift.

FORMULAS FOR SPECIFIC SHIFT IN CARBON

In evaluating the shift in the spectral line

$$2p^2\,{}^1S_0-2p3s\,{}^1P_1$$

of neutral carbon, it is necessary to obtain the shifts in the terms $2p^2\,{}^1S$ and $2p3s\,{}^1P$. There are three terms which arise from the configuration $2p^2$. These are ${}^1D$, ${}^1S$, and ${}^3P$. An expression for the shift in the ${}^1S$ term can be found from Slater's diagonal sum rule. The shift for ${}^1D$ can be readily calculated by observing that the electronic state $2p(m_s=\frac{1}{2},\ m_l=1)2p(m_s=-\frac{1}{2},\ m_l=1)$ belongs only to this term. Evaluation of the double sum leads to

$$\bar{\sigma}=(M_1^{-1}-M_2^{-1})(\tfrac{2}{3}mRy)[2J^2(2p,1s)+2J^2(2p,2s)]. \quad (1)$$

TABLE I. Specific isotope shift of C^{13} relative to C^{12} in cm^{-1}.

Term	M.Y.H. functions	Hartree functions without exchange	Hartree-Fock functions with exchange
$2p^2\,{}^1S$	···	0.908	1.000
$2p^2\,{}^3P$	0.893	0.908	1.064
$2p3s\,{}^1P$	···	0.591	···

The electronic state $2p(m_s=\frac{1}{2}, m_l=0)2p(m_s=\frac{1}{2}, m_l=1)$ appears only in the ${}^3P$ term and the shift for this term can be shown to be the same as (1). There are three electronic states for which $\sum m_s=0$, $\sum m_l=0$, and according to the diagonal sum rule the sum of the shifts of all three electronic states, less the shift of the ${}^3P$ and ${}^1D$ gives the shift of the ${}^1S$. The shift of the ${}^1S$ can also be shown to be the same as (1) and so the expressions for the shift of all three terms have the same form. The shift of the $2p3s\,{}^1P$ term may be found by applying the diagonal sum rule. The electronic state $3s(m_s=\frac{1}{2}, m_l=0)2p(m_s=\frac{1}{2}, m_l=1)$ is present in only the $2p3s\,{}^3P$ term and so the shift for this term is:

$$\bar{\sigma}=(M_1^{-1}-M_2^{-1})(\tfrac{2}{3}mRy)[J^2(2p,1s)+J^2(2p,2s)+J^2(2p,3s)].$$

There are two electronic states for which $\sum m_s=0$, $\sum m_l=0$ and the sum of the shifts for these two states is the same as (1). Therefore, the shift of the ${}^1P$ term is:

$$\bar{\sigma}=(M_1^{-1}-M_2^{-1})(\tfrac{2}{3}mRy)[J^2(2p,1s)+J^2(2p,2s)-J^2(2p,3s)].$$

TABLE II. Values of the J integrals calculated from radial functions.

Term		M.Y.H. functions	Hartree functions without exchange	Hartree-Fock functions with exchange
$2p^2\,{}^1S$	$J(2p,1s)$	···	−1.2301	−1.2949
	$J(2p,2s)$	···	0.5155	0.5297
$2p^2\,{}^3P$	$J(2p,1s)$	−1.1899	−1.2301	−1.3500
	$J(2p,2s)$	0.5766	0.5155	0.5105
$2p3s\,{}^1P$	$J(2p,1s)$	···	−1.4559	···
	$J(2p,2s)$	···	0.4715	···
	$J(2p,3s)$	···	0.1583	···

NUMERICAL CALCULATIONS

There are several types of one-electron radial functions available for the $2p^2$ configuration of neutral carbon. Torrance[7] has computed Hartree numerical functions without exchange and Jucys[8] has computed Hartree-Fock functions with exchange. Analytic functions of the Morse, Young, and Haurwitz type (M.Y.H.) have also been calculated[9] for the ${}^3P$ term only. The shifts for both the $2p^2\,{}^1S$ and $2p^2\,{}^3P$ terms have been calculated using these functions. The results are tabulated in Table I. As previously mentioned, the expressions for the $2p^2\,{}^3P$ and $2p^2\,{}^1S$ shifts are the same; the difference in numerical results in the case of the Hartree-Fock functions is due to a difference in the wave functions for the two terms. In the case of the Hartree functions without exchange, there is no distinction between terms of a given electron configuration. The Hartree-Fock and M.Y.H. functions are inherently

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[7] C. C. Torrance, Phys. Rev. **46**, 388 (1934).

[8] A. Jucys, Proc. Roy. Soc. (London) **173**, 59 (1939).

[9] W. E. Duncanson and C. A. Coulson, Proc. Roy. Soc. (Edinburgh) **62**, 37 (1944).

orthonormal, but the Hartree functions without exchange must be orthogonalized by taking linear combinations as follows:

$$R_0(1s)=R(1s),$$
$$R_0(2s)=1.0006R(2s)-0.03552R(1s).$$

It is not necessary to modify $R(2p)$ since the angle functions produce orthogonality to the s electron functions.

There were no radial functions available for the $2p3s$ configuration so it was decided to calculate Hartree functions without exchange. It was also necessary to orthogonalize these functions as follows:

TABLE III. Specific isotope shift of C^{14} relative to C^{12} in cm^{-1}.

Term	M.Y.H. functions	Hartree functions without exchange	Hartree-Fock functions with exchange
$2p^2\,{}^1S$	···	1.686	1.857
$2p^2\,{}^3P$	1.658	1.686	1.976
$2p3s\,{}^1P$	···	1.098	···

$$R_0(1s)=R(1s),$$
$$R_0(2s)=1.0007R(2s)-0.03703R(1s),$$
$$R_0(3s)=1.0050R(3s)-0.09879R(2s)-0.00623R(1s).$$

The calculated shift for the ${}^1P$ term is also given in Table I.

The values of the J integrals calculated with the orthogonalized Hartree functions as well as with the Hartree-Fock and M.Y.H. functions are shown in Table II. Numerical integration was used in the calculations involving Hartree and Hartree-Fock functions.

It is possible to compute the shift of C^{14} relative to C^{12} merely by putting the appropriate masses in the formulas. The results obtained are listed in Table III.

From the term shifts computed above, with Hartree functions, the shift in the transition can be readily computed. The results are tabulated with experimental values, in Table IV.

TABLE IV. Comparison of experimental and calculated shifts for the transition $2p^2\,{}^1S-2p3s\,{}^1P(\lambda=2478.5\text{A})$ in cm^{-1}.

	C^{13} relative to C^{12}	C^{14} relative to C^{12}
Experimental shift	-0.156 ± 0.002	-0.294 ± 0.002
Normal shift	0.141	0.261
Experimental specific shift	-0.297	-0.555
Calculated specific shift	-0.317	-0.588

The discrepancy between the experimental and calculated specific shifts is 0.020 cm^{-1} for the $C^{12}-C^{13}$ case. The effect of exchange on the shift of the $2p^2\,{}^1S$ term is 0.092 cm^{-1}, which is larger than the discrepancy and indicates that the inclusion of exchange in the calculations may improve the transition results. However, there are no Hartree-Fock functions available at present for the $2p3s\,{}^1P$ term. If the $2p^2\,{}^1S$ term shift calculated with Hartree-Fock function is used with the $2p3s\,{}^1P$ term shift calculated with Hartree functions, the transition specific shift is -0.409 cm^{-1}. This is in poorer agreement with the experimental value than when Hartree functions are used for both terms. It appears from this, that it is not advisable in such calculations to mix the types of functions used.

A calculation of the $C^{12}-C^{13}$ specific shift was made with the assumption that the $1s$ and $2s$ Hartree radial functions are the same for the $2p3s$ configuration as for the $2p^2$ configuration. The value of the transition shift obtained is -0.460 cm^{-1}. It is apparent that such an assumption is not justified in the case of these terms of carbon.

At present, work is proceeding on a calculation of Hartree-Fock functions for the $2p3s\,{}^1P$ term of carbon. It is hoped that the use of this type of function for both terms will improve the agreement between experimental and calculated shift for the $2p^2\,{}^1S-2p3s\,{}^1P$ transition.

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