ISOTOPE SHIFT OF $1s-2p$ AND $2p-2s$ LINES IN NeI SPECTRUM

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The values of specific isotope shift of the $1s-2p$ and $2p-2s$ lines in the NeI spectrum are calculated. Intermediate coupling in the neon atom is accounted for by using coupling coefficients and peculiar wave functions. The calculated values correspond fairly well with experimental data.

1. Introduction

An atom consisting of a nucleus of finite mass and electronic shell composed of two or more (N) electrons is described by a Hamiltonian of the form

$$\hat{H} = -\hbar^2\left[\frac{1}{2\mu}\sum_{i=1}^{N}\nabla_i^2+\frac{1}{M}\sum_{i>j}\nabla_i\cdot\nabla_j\right]+V \tag{1}$$

where $\mu = mM/(m+M)$ is the reduced electron mass, and V is the operator of electrostatic interactions in the atom. It is evident from the form of the Hamiltonian that to the energy eigenvalue found by the central field approximation two corrections must be added. The first, proportional to the value of the term, is known as the mass isotopic effect and expressed by the formula

$$N = T-T_\infty = -T_\infty\frac{m}{M} \tag{2}$$

where T_∞ and T respectively denote the value of the term in the central field approximation and after the finite nucleus mass is considered.

The other correction depends very strongly on the state of the electronic shell and is directly associated with the correlation of the momenta of the electrons in the atom. It is called the specific mass isotopic effect and may be calculated by the first approximation of perturbation theory. This procedure is well-founded, for the isotope shifts of terms are much smaller than the terms themselves. In the one-electron approximation the

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atomic wave function is assumed to be the product of normalized one-electron functions $\Psi = \prod_{k=1}^{N} f_k$. With due consideration of the normality of the wave function at infinity we get for the specific effect the following expression:

$$\sigma = -\frac{\hbar^2}{M} \sum_{i>j} \int \Psi^* \nabla_i \nabla_j \Psi d\tau =$$

$$= \frac{\hbar^2}{M} \sum_{i>j} \int f_j^* \nabla_i f_i^* f_i \nabla_j f_j d\tau_i d\tau_j \,. \tag{3}$$

Condon and Shortley [1] have given formulae for matrix elements of a quantity symmetrical in indices $\sum_{ij} g(i, j)$ corresponding to our operator. We write the wave function in the form of a determinant ensuring proper symmetry and take under consideration two functions differing by at most two sets of quantum numbers. We then obtain for the matrix elements of σ the expressions

$$\langle \alpha|\sigma|\alpha\rangle = \frac{\hbar^2}{M} \sum_{i>j} |\langle f_i|\nabla|f_j\rangle|^2 \delta(m_s^i, m_s^j) \tag{4}$$

$$\langle \alpha|\sigma|\beta\rangle = -\frac{\hbar^2}{M} [\langle f_r|\nabla|f_{r'}\rangle \langle f_t|\nabla|f_{t'}\rangle \delta(m_s^r, m_s^{r'}) \delta(m_s^t, m_s^{t'}) -$$

$$- \langle f_r|\nabla|f_{t'}\rangle \langle f_t|\nabla|f_{r'}\rangle \delta(m_s^r, m_s^{t'}) \delta(m_s^t, m_s^{r'}) \tag{5}$$

where f_k stands for the one-electron function, and α and β are two different functions of the atom. With the selection rule $\Delta m_l = 0, \pm 1$ and $\Delta l = 1$ taken into account, we get only three matrix elements:

$$-\hbar^2 |\langle n, l, m_l|\nabla|n', l-1, m_l\rangle|^2 = \frac{(l^2 - m_l^2) 2m\,Ry}{(2l+1)(2l-1)} J^2(n, l; n', l-1) \tag{6}$$

$$-\hbar^2 |\langle n, l, m_l|\nabla|n', l-1, m_l \mp 1\rangle|^2 = \frac{(l \pm m_l - 1)(l \pm m_l) 2m\,Ry}{2(2l+1)(2l-1)} J^2(n, l; n', l-1) \tag{7}$$

where

$$J(n, l; n', l-1) = \int_0^\infty \frac{P(n, l)}{r} \left[r \frac{dP(n', l-1)}{dr} - lP(n', l-1) \right] dr \,. \tag{8}$$

In the latter expression the integrand is a radial function of normalization $\int_0^\infty P^2 dr = 1$.

Formula (1) indicates the essential role of the angle between the radius vectors of the electrons in the atom expressed by the scalar product $\nabla_i \cdot \nabla_j$. Correlation of electron momenta leads on the one hand to the emergence of the specific mass isotopic effect,

whereas on the other it finds expression in the shape of the radial wave functions describing the atom's state. It should be noted that the correlation of electron momenta is introduced into the Hamiltonian not by the angles of phase shift between the electron radius vectors, but by the distances r_{ik} between the i-th and k-th electrons, which *via* electrostatic interaction between the electrons affects in the end the shape of the radial functions. This evident relationship allows the specific isotopic effect to be regarded as a criterion for verifying wave functions from the point of view of correlation of electron momenta in the atom [10].

2. *Calculation of the specific effect in* NeI *atom for the pair of stable isotopes* ^{20}Ne *and* ^{22}Ne

In this paper we present the calculated specific isotope effect for transitions between the configurations $2p^5 3s$, $2p^5 3p$ and $2p^5 4s$. To be able to calculate the integrals $J(n, l; n', l-1)$ for these transitions there must be available the wave functions of the ground state and the excited states $3s$, $3p$ and $4s$. The wave functions of the $1s$, $2s$ and $2p$ states were adopted from the paper by Gold and Knox [13]. They concern the excited state of the NeI atom in which one of the $2p$ electrons transited to the $3s$ orbit. These functions were also applied in the case of higher excited states, assuming that when transitions proceed to orbits higher than $3s$ changes in the core are negligible. The wave function of the $3p$ state has been calculated by Brown and published in the paper by Bartlett and Gibbons [2]. These functions have already been used in calculations in earlier theoretical studies. But for the excited states $3s$ and $4s$ the functions used here are new ones.

For the $2p^5 3s$ configuration the functions were calculated on the basis of data published by Vainshtain and Minaeva [6]. In their paper they give the coefficients of expansion of wave functions of intermediate couplings into a combination of functions in the $L-S$ coupling. These functions, therefore, take the form

$$\Psi_{\bar{\Gamma}} = \sum_{L,S} (\bar{\Gamma}/\Gamma)\Psi_{\Gamma} \tag{9}$$

where Ψ_{Γ} are the initial $L-S$ functions, Γ is the set of quantum numbers $(\gamma\,[S_p L_p]\tfrac{1}{2} l\;[SL]\,J)$, and $\bar{\Gamma}$ is the index of the wave function corresponding to the intermediate coupling.

The expansion coefficients $(\bar{\Gamma}/\Gamma)$ are given in Table I. The last column illustrates the orthogonality of the matrix of coefficients.

TABLE I

Expansion coefficients of wave functions

	$^3P_2$	$^3P_1$	$^1P_1$	$^3P_0$	$\sum_{\Gamma} (\bar{\Gamma}/\Gamma)^2$
$^3\bar{P}_2$	1	—	—	—	1
$^3\bar{P}_1$	—	0.964	0.266	—	1.00005
$^1\bar{P}_1$	—	−0.266	0.964	—	1.00005
$^3\bar{P}_0$	—	—	—	1	1

The initial functions were those of Gold and Knox for the terms $3s(^3P)$ and $3s$ (^1P). They were calculated by the Hartree-Fock method employing the $2p^6$ $(^1S_0)$ functions of NeI as trial functions.

Since wave functions of higher excited states of neon are hitherto unavailable in the literature, the required function was computed by the Hartree-Fock-Slater method in the analytical approximation of the Herman and Skillman method. Use was made of the program described in Ref. [5]. This function had the form $\sum_i a_i r^{n_i} e^{-\alpha_i r}$, where n_i are positive

TABLE II

Values of $4s$ state wave function of neutral neon calculated for virtual state

r	$4s(^3P, ^1P)$	r	$4s(^3P, ^1P)$	r	$4s(^3P, ^1P)$	r	$4s(^3P, ^1P)$
0.00	0.0000	0.35	−0.0523	0.70	−0.0766	1.60	0.0832
1	0.0114	6	−0.0552	1	−0.0757	1.73	0.1045
2	0.0204	7	−0.0579	2	−0.0747	1.86	0.1239
3	0.0275	8	−0.0605	3	−0.0736	1.98	0.1414
4	0.0328	9	−0.0629	4	−0.0725	2.00	0.1430
5	0.0366	0.40	−0.0652	5	−0.0714	2.24	0.1689
6	0.0392	1	−0.0673	6	−0.0702	2.50	0.1881
7	0.0406	2	−0.0692	7	−0.0689	2.75	0.1992
8	0.0410	3	−0.0710	8	−0.0676	3.00	0.2030
9	0.0406	4	−0.0727	9	−0.0663	3.26	0.2002
0.10	0.0395	5	−0.0742	0.80	−0.0649	3.52	0.1915
1	0.0377	6	−0.0756	1	−0.0635	3.78	0.1776
2	0.0354	7	−0.0769	2	−0.0621	4.00	0.1618
3	0.0327	8	−0.0780	3	−0.0606	4.54	0.1118
4	0.0295	9	−0.0790	4	−0.0591	5.00	0.0612
5	0.0260	0.50	−0.0799	5	−0.0576	5.57	−0.0073
6	0.0223	1	−0.0806	6	−0.0560	6.00	−0.0599
7	0.0183	2	−0.0813	7	−0.0544	6.59	−0.1287
8	0.0142	3	−0.0818	8	−0.0528	7.00	−0.1719
9	0.0100	4	−0.0822	9	−0.0511	8.0	−0.2582
0.20	0.0057	5	−0.0825	0.90	−0.0494	9.0	−0.3135
1	0.0014	6	−0.0827	1	−0.0478	10.0	−0.3340
2	−0.0030	7	−0.0828	2	−0.0460	11.0	−0.3430
3	−0.0073	8	−0.0828	3	−0.0443	12.0	−0.3292
4	−0.0116	9	−0.0827	4	−0.0425	13.0	−0.3045
5	−0.0159	0.60	−0.0825	5	−0.0408	14.0	−0.2738
6	−0.0201	1	−0.0823	6	−0.0390	15.0	−0.2407
7	−0.0242	2	−0.0819	7	−0.0371	16.0	−0.2078
8	−0.0281	3	−0.0815	8	−0.0353	17.0	−0.1767
9	−0.0320	4	−0.0810	9	−0.0335	18.0	−0.1483
0.30	−0.0357	5	−0.0805	1.00	−0.0316	19.0	−0.1230
1	−0.0393	6	−0.0798	1.09	−0.0148	20.0	−0.1011
2	−0.0428	7	−0.0791	1.22	0.0105	25.0	−0.0335
3	−0.0461	8	−0.0784	1.34	0.0357	30.0	−0.0092
4	−0.0493	9	−0.0775	1.47	0.0605	35.0	−0.0020
						40.0	−0.0003

integers. Some of the expansion coefficients a_i, n_i and α_i were adopted from the paper by Allen [3]. Since Allen's expansion proved to be a good approximation only for orbitals occupied in the ground state, this expansion has been extended to include terms of the type $r^{n_i}e^{-\alpha_i r}$, where the parameters n_i (= 3, 4) and α_i were determined with the use of Slater's rule for orbitals of excited atoms. The expansion coefficients $a_i (i = 1, \ldots, 12)$ were found by the variational method. In this way a basis numbering 12 initial functions was obtained. It should be emphasized that the wave function of the excited state $4s$ acquired by this procedure does not account for changes in the electronic core at excitation of the atom. The numerical values of this function are given in Table II.

When calculating the specific effect account was taken of the intermediate coupling occuring in neon by using Stone's X-parameters [4], which define the contribution of a given level ns_i (Paschen notation) to the total isotopic effect. The values of these parameters are given in Table III.

TABLE III

Values of X-parameters

Level	ns_2	ns_3	ns_4	ns_5
$X(n = 1)$	0.380	1	0.953	1
$X(n = 2)$	0.593	1	0.741	1

Changes in the $1s^2 2s^2 2p^5$ core of electrons at transitions of a valence electron are allowed for in the constants A and B. They are calculated by normalizing theoretical results to experimental data for one of the transitions. The specific effect was computed from the following formulae:

$$\sigma(1s_2 - 2p) = \frac{2m\ \mathrm{Ry}\ \Delta M}{M_1 M_2}\left\{A + \frac{1}{3}[J^2(3p, 1s) + J^2(3p, 2s)] - \right.$$

$$\left. - X \cdot J^2[2p, 3s(^1P)]\right\} \tag{10}$$

$$\sigma(1s_i - 2p) = \frac{2m\ \mathrm{Ry}\ \Delta M}{M_1 M_2}\left\{A + \frac{1}{3}[J^2(3p, 1s) + J^2(3p, 2s)] - \right.$$

$$\left. - X \cdot J^2[2p, 3s(^3P)]\right\} \quad (i = 3, 4, 5) \tag{11}$$

$$\sigma(2p - 2s_i) = \frac{2m\ \mathrm{Ry}\ \Delta M}{M_1 M_2}\left\{B - \frac{1}{3}[J^2(3p, 1s) + J^2(3p, 2s)] + \right.$$

$$\left. + X \cdot J^2(2p, 4s)\right\} \quad (i = 2, 3, 4, 5). \tag{12}$$

The integrals J were calculated by means of a computer. The following results were obtained:

$$\begin{aligned}
J(2p, 1s) &= -2.7996,\\
J(2p, 2s) &= 0.7565,\\
J[2p, 3s(^3P)] &= 0.2991 \text{ (for the } 1s_4 \text{ level)},\\
J[2p, 3s(^3P)] &= 0.2483 \text{ (for } 1s_3 \text{ and } 1s_5 \text{ levels)},\\
J[2p, 3s(^1P)] &= 0.1513,\\
J(2p, 4s) &= 0.1286,\\
J(3p, 1s) &= -0.4412,\\
J(3p, 2s) &= -0.0457.
\end{aligned}$$

These values were put into formulae (10), (11) and (12).

The constant A was calculated for the transitions between the configurations $2p^53p$ and $2p^53s$ by normalizing the theoretical value of the shift for the $1s_4 - 2p$ transition:

$$\sigma(1s_4-2p) = \frac{2\cdot 109737.303\cdot 2}{1836\cdot 20\cdot 22}\left[A+\frac{1}{3}(0.1947+0.0021)-\right.$$

$$\left.-0.953\cdot 0.085\right] = A'+0.0356-0.0463 = .$$

$$= A'-0.0107 \underset{\text{df}}{=} 0.0165 \text{ K}.$$

Whereby $A' = 0.0107+0.0165 = 0.0272$ K. The other shifts are as follows: $\sigma(1s_2-2p) = 0.0272+0.0356-0.5434\cdot 0.38\cdot 0.0229 = 0.0581$ K. The experimental value of the latter shift is 0.0372 K. This mean value is calculated with the exclusion of the transition from the $2p_1$ level owing to the large deviation of this shift from the remaining values. Taking account of Stone's coefficients causes the theoretical values for the ns_3 and ns_5 levels to become identical. We have hence

$$\sigma(1s_3-2p) = \sigma(1s_5-2p) = 0.0628-0.5434\cdot 0.0616 = 0.0293 \text{ K}.$$

The experimental value for the $1s_3-2p$ transition is 0.0148 K, whereas for the $1s_5-2p$ transition 0.0156 K. When the average of these values was being found transitions from the $2p_{10}$ level were disregarded because of the large deviation of this shift from all other values for the remaining $2p$ levels.

The constant B for the $2p_{10}-2s_i$ transitions were calculated by normalizing the shifts of the $2p_{10}-2s_4$ transition:

$$\sigma(2p_{10}-2s_4) = B'-0.5434\cdot 0.656+0.741\cdot 0.009 = B'-0.0289 \underset{\text{df}}{=} 0.014 \text{ K}.$$

Whereby $B' = 0.0289-0.014 = 0.0149$ K. For the other transitions the shifts are as follows:

$$\sigma(2p_{10}-2s_2) = 0.0149-0.0356+0.0593\cdot 0.009 = -0.0154 \text{ K}.$$

The experimental value is -0.021 K.

$$\sigma(2p_{10}-2s_3) = \sigma(2p_{10}-2s_5) = -0.0207+0.009 = -0.0117 \text{ K}.$$

For the $2p_{10}-2s_5$ transition the experimental value is -0.009 K, whereas no experimental data is available for the $2p_{10}-2s_3$ transition.

When calculating the isotope shift of the $2p_4-2s_2$ transition the difference between the experimental data for the $1s_5-2p_{10}$ transition and the mean for the other $1s_5-2p_i$ transitions was accepted as being the same for $2p-2s_i$ transitions. This difference is, according to the data of Odintsov [11], 0.0031 K. Because of this change the constant B' for $2p_i-2s_j$ ($i \neq 10$) transitions takes the value of $B'' = 0.0149+0.0031 = 0.0180$ K. For these transitions, hence, we have

$$\sigma(2p_i-2s_2) = 0.018-0.0356+0.0053 = -0.0123 \text{ K}.$$

The experimental value for the $2p_4-2s_2$ transition is -0.0128 K, after Refs [14, 15]

These results are compared in Table IV. The experimental data for the $2p_{10}-2s$ transitions are taken from Refs [7, 8]. Experimental error is ± 3 mK. The data on the shift for the $2p_4-2s_2$ transition were taken from Refs [14, 15], in which the estimated errors are given as ± 0.1 mK [14] and ± 0.3 mK [15]. For the $1s_i-2p_i$ transitions the

TABLE IV

Comparison of calculated specific isotope shifts with experimental data for ^{20}Ne and ^{22}Ne

Transition	Weighted mean (exp. values) [mK]	Theoretical value	
		present paper [mK]	Gabła [10] [mK]
$1s_2-2p_i$ ($i \neq 1$)	37.2 [7, 8, 9, 11, 12]	58.1	37.55
$1s_2-2p_1$	33.5 [7, 8, 9, 11, 12]	—	—
$1s_3-2p$	14.9 [7, 8, 9, 11, 12]	29.3	14.64
$1s_4-2p$	16.5 [7, 8, 9, 11, 12, 15]	16.5 (norm.)	16.22
$1s_5-2p_i$ ($i \neq 10$)	15.6 [7, 8, 9, 11, 12]	29.3	14.64
$1s_5-2p_{10}$	18.4 [7, 8, 9, 11, 12]	32.4	—
$2p_{10}-2s_5$	− 9 [7, 8]	−11.7	—
$2p_{10}-2s_4$	−14 [7, 8]	−14 (norm.)	—
$2p_{10}-2s_2$	−21 [7, 8]	−15.4	—
$2p_4-2s_2$	−12.8 [14, 15]	−12.3	—

weighted mean is calculated from all experimental results reported in Refs [7, 8, 9, 11, 12, 15]. The weight coefficients were the reciprocal of measurement errors. Table IV also contains the references from which data for calculating the various values were taken.

It must be emphasized that the comparison in Table IV shows a worsening of results for the $1s-2p$ transitions as compared with earlier calculations of Gabła [10]. The same calculative formalism had been used then, the wave functions of Gold and Knox being employed for the $2p^5 3s$ state and those of Brown for the $2p^5 3p$ state. Thus, the values of

the integrals $J(2p, 1s)$, $J(2p, 2s)$, $J(3p, 1s)$ and $J(3p, 2s)$ are identical with those given here, but for $J(2p, 3s)$ the values of 0.2482 and 0.2261 had been obtained for terms ^3P and ^1P, respectively. The existence of intermediate couplings had been accounted for through X-coefficients introduced by Stone. The additive constant due to the core had been determined, as here, by normalization to one of the most reliable experimental results. Although use has been made here of wave functions corresponding to intermediate couplings for the $2p^5 3s$ configuration, in agreement with the results of Vainshtain and Minaeva, the outcome has proved to be in worse agreement with experimental data than before. This may perhaps be caused by the fact that the Vainshtain-Minaeva coefficients were applied to wave functions of terms, and not levels. Functions for levels are unavailable in the literature at present, however.

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