Isotope Shift in Neon

J. H. BARTLETT, JR., AND J. J. GIBBONS, JR., University of Illinois (Received June 16, 1933)

The theory of isotopic displacement due to the motion of the nucleus has been extended to atoms with any number of electrons (assuming Russell-Saunders coupling) and applied to the transitions $2p^5 3s - 2p^5 3p$ in neon. Approximate Hartree wave functions have been obtained and orthogonalized. The theory gives a shift in singlet

INTRODUCTION

HE researches of Schüler and others have demonstrated the existence of isotope shifts in the spectra of H,1 Li,2 Ne,3 Cl,4 K,5 Cu,6 Zn,7 Ba,8 Hg,5 Tl,5 and Pb.5 These observed shifts are in most cases (excepting H) in complete disagreement with those to be expected by simply replacing *m*, the electronic mass, by μ , the equivalent mass, in the Rydberg constant. This places the line emitted by the heavier isotope always at a slightly higher frequency than the corresponding line emitted by the lighter isotope. But experiments⁷ on the lines 7479, 5834, 6215, and 6471 of Zn II give an isotope shift twenty to thirty times too large and in a direction opposite to that predicted by the above method; lines due to the heavier isotopes 68 and 66 lie to the low frequency side of those due to the lighter isotope 64, at about equal intervals (0.08 to 0.10 cm^{-1}). It becomes quite apparent, therefore, that the explanation of these isotope shifts must come from a different quarter.

One possible explanation⁹ is that the external

⁶ R. Ritschl, Zeits. f. Physik 79, 1 (1932).

states of 0.0195 cm⁻¹ more than that in triplet states, as against approximately 0.017 cm⁻¹ measured by Nagaoka and Mishima. However, the calculated shift for the singlet transitions is 0.0038 cm⁻¹, as against the experimental value of 0.0332 cm⁻¹. This discrepancy may disappear if better wave functions are found.

electrons of the atom move in fields which are non-Coulomb near the origin and that the isotope shifts are due to different deviations from the Coulomb field for the different isotopes. One of the writers¹⁰ has made rough calculations for Tl, with the result that the calculated order of magnitude of the shift seemed to be in agreement with that which was observed, provided that certain arbitrary values for the nuclear radii of Tl 203 and of Tl 205 were assigned. These calculations were later improved upon by Racah,¹¹ Rosenthal and Breit,12 and Breit,13 with the result that this theory may in fact provide the explanation of the isotope shifts in Hg, Tl and Pb. However, we have carried through similar calculations for neon and copper, assuming the nuclear radius to vary as the cube root of the mass, and find that the displacement to be expected is much smaller than that which is observed and in the opposite direction. This leads us to the tentative conclusion that isotope shifts in the spectra of heavy elements may be partly explained by changes in nuclear radii but that this is not the explanation in the case of the light elements.

For Li II, Hughes and Eckart¹⁴ were able to account satisfactorily for the observed isotope shift by assuming it to be a mass effect, due to

¹Urey, Brickwedde and Murphy, Phys. Rev. **40**, 1 (1932).

² H. Schüler, Zeits. f. Physik 42, 487 (1927).

⁸ G. Hansen, Naturwiss. 15, 163 (1927).

⁴ S. Tolansky, Zeits. f. Physik 73, 470 (1931).

⁵ H. Schüler, Zeits. f. Physik 76, 14 (1932).

⁷ H. Schüler and H. Westmeyer, Zeits. f. Physik 81, 565 (1933).

⁸ Kruger, Gibbs and Williams, Phys. Rev. 41, 322 (1932).

⁹ Pauling and Goudsmit, *Structure of Line Spectra*, p. 202 (1930).

¹⁰ J. H. Bartlett, Jr., Nature 128, 408 (1931).

¹¹ G. Racah, Nature 129, 723 (1932).

¹² J. E. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932).

¹³ G. Breit, Phys. Rev. 42, 348 (1932).

¹⁴ D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930).

the motion of the nucleus.¹⁵ The present paper extends their work to the general case of an atom with many electrons. The theory is given for Russell-Saunders coupling only, but modifications so that it will apply to other types of coupling may be made just as in the theory of supermultiplets.^{16, 17} Finally, an application to the spectrum of neon is made and approximate agreement with certain observed relative shifts¹⁸ is obtained, even though the deviation from Russell-Saunders coupling is rather appreciable.

THEORY OF ISOTOPE SHIFT

After the center of gravity coordinates have been separated out, the wave equation for a system of N electrons, each of mass m, and one nucleus of mass M is¹⁹

$$-(h^{2}/8\pi^{2})\left\{\frac{1}{\mu}\sum_{k=1}^{N}\nabla_{k}^{2}+\frac{2}{M}\sum_{k< j}\nabla_{k}\cdot\nabla_{j}\right\}\psi+\{V(x)-W\}\psi=0,$$
(1)

where x_k , y_k and z_k are the rectangular coordinates of the kth electron relative to the nucleus, and

$$\mu = mM/(m+M); \qquad (\nabla_k)_x = \partial/\partial x_k. \tag{2}$$

If we know W(m) and $\psi(m)$ for a stationary nucleus, then the value of the energy parameter in Eq. (1) is approximately $W = W(\mu) + \Delta W$, where $W(\mu) = (\mu/m)W(m)$ and

$$\Delta W = -\frac{h^2}{4\pi^2 M} \int \psi^*(m) \bigg[\sum_{k < j} \nabla_k \cdot \nabla_j \bigg] \psi(m) dv.$$

The isotope shift in hydrogen may be accounted for by replacing W(m) by $W(\mu)$. This causes a general contraction of the spectrum which is termed the normal effect. The "specific effect" is measured by ΔW . In the case of neon, the specific effect proves to be of about the same order of magnitude as the normal effect.

The operator $\nabla_j \cdot \nabla_k$ is symmetric in j and k and is thus similar to the electrostatic repulsion $1/r_{jk}$. If $\psi(m)$ be assumed to be a determinant wave function composed of products of single-electron orthogonal wave functions, then the analysis of Slater²⁰ can be used, provided that $\nabla_j \cdot \nabla_k$ be substituted for $1/r_{jk}$. The diagonal energy increment is $-(h^2/4\pi^2 M)\Sigma J(nn') + (h^2/4\pi^2 M)\Sigma K(nn')$, where now

$$J = \int u^*(n/k) u^*(n'/l) \nabla_k \cdot \nabla_l u(n/k) u(n'/l) d\tau_k d\tau_l$$

= $-(4\pi^2/h^2) \{ (n'/p_x | n')(n | p_x | n) + (n' | p_y | n')(n | p_y | n) + (n' | p_z | n')(n | p_z | n) \}$

=0, (since the diagonal elements of the momentum matrix vanish);

and

$$K = \int u^*(n/k) u^*(n'/l) \nabla_k \cdot \nabla_l u(n/l) u(n'/k) d\tau_k d\tau_l$$

= -(4\pi^2/h^2) { (n | \psi | n')(n' | \psi | n) + (n | \psi | n')(n' | \psi | n) + (n | \psi | n')(n' | \psi | n) }.

 15 We are deeply indebted to Dr. Racah, who informed one of us (J. H. B., Jr.) of the possibility of such an explanation.

¹⁶ W. V. Houston, Phys. Rev. 33, 297 (1929).

¹⁷ J. H. Bartlett, Jr., Phys. Rev. **34**, 1253 (1929); **35**, 229 (1930) and subsequent papers by M. H. Johnson, Jr.

¹⁸ H. Nagaoka and T. Mishima, Inst. of Phys. and Chem. Research, Tokyo 13, 293 (1930).

¹⁹ This equation has been given by Hughes and Eckart (ref. 14) and is in accord with classical theory. See Whittaker, *Analytical Dynamics*, p. 344 (1927).

²⁰ J. C. Slater, Phys. Rev. 34, 1304 (1929).

Since the momentum matrices are Hermitian, K is intrinsically negative. The specific effect ΔW is thus also intrinsically negative and in inverse proportion to the nuclear mass. The result is that the energy of each state is made lower, that of the lighter isotope more so than that of the heavier. Whether or not this tends to increase or decrease the frequency of any line emitted by an atom cannot be determined without actually calculating the K's of the states involved.

The summation of K's is taken over all pairs of sets of one-electron quantum numbers $(n, l, m_l, m_s, n', l', m_l', m_s')$. In order that K be different from zero, we must have $m_s' = m_s$ and $l' = l \pm 1$, since K depends on the momentum matrices. In fact, the K's are (with constant frequency) proportional to the intensities, so that we may write²¹

$$K(m_l, l; m_l \pm 1, l-1) = C(l, l-1) \{ \frac{1}{2} (l \mp m_l) (l \mp m_l - 1) \},$$

$$K(m_l, l; m_l, l-1) = C(l, l-1) (l^2 - m_l^2).$$

The value of C(l, l-1) is determined most conveniently for the case $m_l \rightarrow m_l$. Putting $u = N_l R_{nl} P_l^{m_l} e^{im_l \varphi}$, where $P_l^{m_l}$ is the associated Legendre polynomial as defined by Darwin²³ and N_l is the normalization constant (assuming R_{nl} to be normalized), we have²²

$$K(m_{l}, l; m_{l}, l-1) = \int u^{*}(n, l, m_{l}) \frac{\partial}{\partial z} u(n', l-1, m_{l}) dv \cdot \int u^{*}(n', l-1, m_{l}) \frac{\partial}{\partial z} u(n, l, m_{l}) dv = I_{z_{1}} I_{z_{2}} \text{ (say)}.$$

According to Darwin²³

$$\frac{\partial}{\partial z} f P_{l}^{m_{l}} = \frac{1}{2l+1} \left\{ \left(\frac{df}{dr} - \frac{l}{r} f \right) P_{l+1}^{m_{l}} + (l^{2} - m_{l}^{2}) \left(\frac{df}{dr} + \frac{l+1}{r} f \right) P_{l-1}^{m_{l}} \right\},$$

where f is any function of the radius alone.

Then

and

$$I_{z_{2}} = \left(\frac{l^{2} - m_{l}^{2}}{(2l-1)(2l+1)}\right)^{\frac{1}{2}} \left\{ (l+1)\int R_{n', l-1}(1/r)R_{n, l}r^{2}dr + \int R_{n', l-1}\frac{d}{dr}R_{n, l}r^{2}dr \right\}$$
$$I_{z_{1}} = \left(\frac{l^{2} - m_{l}^{2}}{(2l-1)(2l+1)}\right)^{\frac{1}{2}} \left\{ -(l-1)\int R_{n, l}(1/r)R_{n', l-1}r^{2}dr + \int R_{n, l}\frac{d}{dr}R_{n', l-1}r^{2}dr \right\}.$$

Now, for any two radial eigenfunctions R_1 and R_2 ,

$$\int_{0}^{\infty} R_{1}(2/r)R_{2}r^{2}dr + \int_{0}^{\infty} R_{1}\frac{dR_{2}}{dr}r^{2}dr + \int_{0}^{\infty} R_{2}\frac{dR_{1}}{dr}r^{2}dr = r^{2}R_{1}R_{2}\Big|_{0}^{\infty} = 0,$$

since each of the functions R_1 and R_2 must approach zero more rapidly than (1/r) as $r \to \infty$. Hence $I_{z_1} = -I_{z_2}$ and

$$C(l, l-1) = -\frac{\{(l-1)\int R_{nl}(1/r)R_{n', l-1}r^2dr - \int R_{n', l-1}(dR_{nl}/dr)r^2dr\}^2}{(2l-1)(2l+1)}.$$

Incidentally, we may note that, if a single *d*-electron (for example) interacts with a closed shell of p-electrons, the isotopic shift will be independent of the magnetic quantum number associated with the *d*-electron, owing to the Zeeman effect sum-rules.²¹

540

²¹ See W. Pauli, *Handbuch der Physik* XXIII, p. 67 (1926).

sitate a knowledge of the various Hartree potentials. We wish to thank Professor G. Breit for the opportunity of discussing these points with him.

²² As a check on the accuracy of the numerical calculations, one might find it convenient to use relations of the type $(n | p_x | n') = 2\pi i m \nu(n, n')(n | x | n')$. This would necess

²³ C. G. Darwin, Proc. Roy. Soc. A118, 668 (1928).

ISOTOPE SHIFT IN NEON

The total specific shift in the $2p^5 3p$ states is 5K(1s, 2p) + 5K(2s, 2p) + K(1s, 3p) + K(2s, 3p). This shift is characteristic of all the states of the configuration, whether they be of singlet or of triplet type.²⁴

A different situation is present in the case of the $2p^5$ 3s configuration. The energy 5K(1s, 2p)+5K(2s, 2p) occurs just as before, and will be regarded as an additive constant, since numerical calculations show that the 2p wave function (and, by analogy, the 2s function) do not change appreciably from the $2p^5$ 3p to the $2p^5$ 3s configuration. For $M_L=1$, $M_S=1$, the remaining energy is then 3K(2p, 3s), which is the ΔW of the ³P state. For $M_L=1$, $M_S=0$, there are two states, each with a shift 2K(2p, 3s). Applying the energy sum-rules, the ΔW for the ¹P state must then be K(2p, 3s), so that the difference between the ¹P and ³P specific shifts is 2K(2p, 3s).

To obtain an approximation to the 2s and 2pfunctions for the configurations $2p^5 3s$ and $2p^5 3p$, the ground state functions as calculated by Dr. F. W. Brown²⁵ were used as a starting-point. The 3s and 3p functions were found²⁶ (assuming the core functions to be those of the ground state) and are given in Table I. The new field for the core electrons was assumed to be that obtained by subtracting off the field of one of the 2pelectrons and adding on the field of the 3s or 3pelectron. The $2p(2p^5 3s)$ and $2p(2p^5 3p)$ functions were found to be identical (in this approxi-

TADIE	T	Hartree	functions	for	configurations	2.15	35	and 2	15	310	in	neon
TABLE	1.	mannee	junctions	101	conjigurations	ωp	0.0	unu z	P	JP	v ri	neon.

				********		the second best best for described											
r	P(3s)	ξ(3s)	P'(3s)	P(3p)	P(2s)	\xi (2s)	P'(2s)	P(2p)	r	P(3s)	$\eta(3s)$	P'(3s)	P(3p)	P(2s)	$\eta(2s)$	P'(2s)	P(2p)
$\begin{array}{c} 0.00\\ 0.01\\ 0.02\\ 0.03\\ 0.04\\ 0.05\\ 0.06\\ 0.07\\ 0.08\\ 0.09\\ 0.00\\ 0.09\\ 0.00\\ 0.09\\ 0.00\\ 0.09\\ 0.00\\ 0.09\\ 0.00\\ 0.09\\ 0.00\\$	$\begin{array}{c} 0.000\\ .026\\ .046\\ .046\\ .064\\ .076\\ .097\\ .007$	10.000 10.146 10.304 10.489 10.704 11.239 11.576 11.973 12.440 12.994	$\begin{array}{c} -0.414\\527\\622\\702\\768\\901\\927\\944\\961\\955\\935\\935\\935\\935\\935\\935\\935\\935\\935\\935\\935\\935\\935\\377\\262\\2158\\109\\155\\109\\155\\109\\155\\156\\155\\ $	$\begin{array}{c} 0.000\\ .000\\ .000\\ .001\\ .004\\ .008\\ .013\\ .016\\ .025\\ .029\\ .039\\ .049\\ .054\\ .049\\ .058\\ .063\\ .068\\ .063\\ .068\\ .063\\ .073\\ .073\\ .039\\ .049\\ .058\\ .063\\ .068\\ .063\\ .073\\ .073\\ .073\\ .086\\ .093\\ .110\\ .124\\ .139\\ .143\\ .146\\ .133\\ .156\\ .155\\ .155\\ .155\\ .155\\ .155\\ .155\\ .155\\ .155\\ .155\\ .155\\ .155\\ .155\\ .155\\ .153\\ .151\\ .149\\ .148\\ .143\\ .140\\ .138\\ .140\\ .140\\ .138\\ .140\\ .140\\ .138\\ .140\\ .140\\ .138\\ .140$	$\begin{array}{c} 0.000\\ .135\\ .243\\ .243\\ .329\\ .394\\ .442\\ .475\\ .503\\ .501\\ .473\\ .475\\ .503\\ .501\\ .473\\ .479\\ .495\\ .501\\ .473\\ .449\\ .421\\ .495\\ .501\\ .473\\ .449\\ .449\\ .491\\ .474\\ .491\\ .473\\ .449\\ .219\\ .124\\ .421\\ .227\\ .102\\ .124\\ .027\\ .102\\ .124\\ .027\\ .102$	10.000 10.139 10.298 10.478 10.686 10.926 11.207 11.534 11.916 12.367 12.902 13.544	$\begin{array}{c} -0.643\\ -1.424\\ -2.106\\ -2.687\\ -3.678\\ -3.590\\ -3.932\\ -4.212\\ -4.437\\ -4.924\\ -4.924\\ -4.904\\ -4.800\\ -4.424\\ -4.904\\ -4.800\\ -4.424\\ -4.800\\ -4.424\\ -4.800\\ -3.626\\ -3.337\\ -3.045\\ -2.743\\ -2.475\\ -2.203\\ -1.689\\ -1.54\\ -1.228\\ -1.689\\ -1.689\\ -1.689\\ -1.689\\ -3.133\\ -1.689\\ -3.133\\ -1.688\\ -3.168\\ -3.313\\ -3.168\\ -3.333\\ -3.844\\ -3.644\\ -3.664\\ -3.332\\ -3.684\\ -3.683\\ -3.684\\ -3.683\\ -3.684\\ $	$\begin{array}{c} 0.000\\ .003\\ .003\\ .001\\ .003\\ .011\\ .024\\ .040\\ .059\\ .082\\ .106\\ .133\\ .161\\ .190\\ .250\\ .282\\ .313\\ .376\\ .407\\ .469\\ .469\\ .499\\ .499\\ .499\\ .499\\ .558\\ .613\\ .376\\ .407\\ .407\\ .469\\ .499\\ .499\\ .558\\ .613\\ .376\\ .407\\ .407\\ .407\\ .409\\ .499\\ .558\\ .613\\ .376\\ .407\\ .409\\ .409\\ .409\\ .409\\ .400\\ .874\\ .904\\ .993\\ .007\\ .1019\\ .028\\ .003\\ .007\\ .019\\ .0028\\ .003\\ .004\\ .003\\ .003\\ .003\\ .003\\ .003\\ .003\\ .993\\ .003\\ .003\\ .003\\ .983\\ .003\\ .983\\ .003\\ .983\\ .003\\ .983\\ .003\\ .998\\ .003\\ .983\\ .003\\ .998\\ .003\\ .983\\ .003\\ .998\\ .003\\ .0$	$\begin{array}{c} .80\\ .826\\ .904\\ .98\\ 1.0\\ .98\\ 1.0\\ .98\\ 1.1\\ 1.2\\ .98\\ 1.0\\ .98\\ 1.0\\ .98\\ 1.1\\ 1.3\\ 1.4\\ 1.5\\ 1.6\\ 2.2\\ .24\\ 2.6\\ 2.8\\ 3.0\\ 5.5\\ 6.0\\ 5.5\\ 6.5\\ 0.0\\ 10\\ .13\\ .14\\ .15\\ .16\\ .17\\ .18\\ .19\\ .20\\ .22\\ .24\\ .26\\ .27\\ .\end{array}$	$\begin{array}{c} -0.167\\161\\149\\135\\120\\105\\056\\013\\ .031\\ .031\\ .074\\ .116\\ .156\\ .196\\ .196\\ .230\\ .264\\ .230\\ .264\\ .135\\ .351\\ .397\\ .434\\ .444\\ .486\\ .512\\ .332\\ .434\\ .446\\ .512\\ .332\\ .434\\ .446\\ .512\\ .332\\ .434\\ .446\\ .512\\ .332\\ .425\\ .242\\ .382\\ .333\\ .285\\ .242\\ .202\\ .168\\ .382\\ .382\\ .333\\ .333\\ .382\\ .333\\ .333\\ .382\\ .333\\ .333\\ .382\\ .333\\ .3$	$\begin{array}{c} 0.221\\ .262\\ .344\\ .363\\ .395\\ .408\\ .429\\ .446\\ .460\\ .472\\ .482\\ .491\\ .516\\ .521\\ .529\\ \end{array}$	$\begin{array}{c} 0.276\\ .296\\ .328\\ .354\\ .377\\ .394\\ .403\\ .429\\ .438\\ .435\\ .425\\ .410\\ .391\\ .376\\ .301\\ .348\\ .325\\ .301\\ .254\\ .209\\ .002\\ .007\\040\\077\\095\\ \end{array}$	$\begin{array}{c} 0.135\\ .131\\ .125\\ .117\\ .110\\ .102\\ .094\\ .077\\ .054\\ .037\\ .007\\ .016\\064\\ .007\\ .006\\100\\064\\ .007\\ .008\\108\\086\\108\\086\\108\\086\\108\\130\\310\\3$	$\begin{array}{c} -1.071\\ -1.059\\ -1.033\\ -1.003\\970\\935\\972\\935\\972\\550\\480\\480\\412\\300\\216\\154\\108\\015\\002\\001\\002\\001\\000$	0.568 686 7900 8822 901 1.268 1.360 1.433 1.544 1.584 1.621 1.652 1.760 1.788 1.811 1.831 1.831 1.834 1.923	0.539 .603	0.971 953 933 905 876 846 831 754 606 6539 282 246 136 606 136 606 132 282 246 140 104 007 057 024 005 005 005 000

²⁴ This statement embodies the implicit assumption of Russell-Saunders coupling, which is decidedly not the case for this configuration. ²⁵ F. W. Brown, Phys. Rev. 44, 214 (1933).

²⁶ This was done by Dr. Brown, to whom we express our deep appreciation for his assistance. mation) to four figures, and so the $2s(2p^5 3p)$ function was not calculated, but was taken equal to the $2s(2p^5 3s)$ function. These functions are also listed in Table I. Finally, the necessary information for the 1s function is given in Table II.

TABLE II.

P(1s) for neon. $\epsilon = 65.68$.

r	P(1s)	ξ(1s)	$\eta(1s)$
0.00	0.000	10.000	
.01	.541	9.970	
.02	.996	9.940	
.03	1.352	9.910	
.04	1.636	9.878	
.06	2.016	9.817	
.08	2.208	9.760	
.10	2.275	9.709	
.12	2.248	9.665	
.14	2.164	9.623	
.16	2.041	9.584	
.18	1.895	9.549	
.20	1.743	9.517	4.517
.25	1.363	9.444	5.444
.30	1.016	9.388	6.055
.35	0.745	9.329	6.472
.40	.534	9.279	6.779
.50	.264	9.181	7.181
.60	.128	9.094	7.427
.70	.057	9.013	7.584
.80	.028	8.942	7.692
.90	.001	8.878	7.767
1.0	.000		7.817

$$\begin{aligned} \epsilon_{2s}(2p^5 \quad 3s) = 4.11; \quad \epsilon_{2p}(2p^5 \quad 3s) = 2.82; \quad \epsilon_{2p}(2p^5 \quad 3p) = 2.96; \\ \eta = -P'/P; \quad \xi = \eta + (l+1)/r. \end{aligned}$$

The integrations were all carried out numerically. This proved to be the most rapid method available.²⁷ The value of R_{nl} may be found very readily from the ξ , η , and P' values of the Hartree functions.

As an independent check on the wave functions here given, the single-electron 2p function for Ne⁺ was determined by stretching that of O⁺, the stretching factor being that which would bring the positions of the principal maxima of the unionized atoms into coincidence.²⁸ Since the K(2p, 3s) integral calculated from the above 2pfunction agreed within 2 percent with the integral already determined, the check was deemed sufficient.

Finally, it is essential for accuracy that the functions be orthogonalized. The orthogonalization integrals are:

$$\int P(1s)P(2s)dr = 0.022;$$

$$\int P(2s)P(3s)dr = 0.033;$$

$$\int P(1s)P(3s)dr = 0.0044;$$

$$\int P(2p)P(3p)dr = 0.0649.$$

From this, we obtain (approximately)

$$\begin{split} P_{orth}(2s) &= P(2s) - 0.022P(1s), \\ P_{orth}(3s) &= P(3s) - 0.0329P(2s) - 0.0036P(1s), \\ P_{orth}(3p) &= 1.0021P(3p) - 0.0650P(2p). \end{split}$$

With the original non-orthogonal functions, the *K* integrals are:

$$k(1s, 2p) = -2.750;$$
 $k(2p, 2s) = -0.1388;$
 $k(2p, 3s) = -0.01996;$ $k(2s, 3p) = -0.00131;$
 $k(1s, 3p) = -0.0650.$

When, however, the orthogonal functions are used, the K integrals become

$$K(1s, 2p) = -2.750;$$
 $K(2p, 2s) = -0.1674;$
 $K(2p, 3s) = -0.018;$ $K(2s, 3p) = -0.0033;$
 $K(1s, 3p) = -0.0217.$

These results are all in atomic units, so that the unit of energy is twice the ionization energy of hydrogen (with fixed nucleus) = 219,475 cm⁻¹, and the unit of mass = m, the mass of the electron. The mass of the proton is taken as equal to 1840.

The specific shifts are then easily calculated. In what follows we shall omit the constant additive terms 5K(1s, 2p) + 5K(2s, 2p). For a 3p state, then, the specific shifts are

$$\Delta W_{20} = \frac{-0.0250 \times 219,475}{20 \times 1840} = -0.1491 \text{ cm}^{-1}$$

542

²⁷ The determination of analytic approximations seems to us to consume much time and to be of little practical value, since the Hartree curves must either be fitted differently according to the purpose of the calculation, or else the analytic expressions become quite complicated.

²⁸ F. W. Brown, J. H. Bartlett, and C. G. Dunn, Phys. Rev. 44, 296 (1933).

and

$$\Delta W_{22} = \frac{-0.0250 \times 219,475}{22 \times 1840} = -0.1355 \text{ cm}^{-1}.$$

That is, the net shift $\delta \Delta W = \Delta W_{22} - \Delta W_{20}$ = 0.0136 cm⁻¹. For the $2p^5$ 3s ${}^{1}P$ state, the net shift $\delta \Delta W = 0.0098$ cm⁻¹ and for the $2p^5$ 3s ${}^{3}P$ state, this net shift is 0.0293 cm⁻¹. That is, in a transition $2p^5$ $3p \rightarrow 2p^5$ 3s, the singlet lines will be displaced 0.0195 cm⁻¹ more than the triplet lines.²⁹

Comparison with experiment

Nagaoka and Mishima¹⁸ have measured the total isotope shifts and subtracted off the calculated normal shifts to obtain the specific effects. They obtain the results in Table III.

TABLE III.

	Range of specific shift	Ave.		
$ \frac{1s_2-2p}{1s_3-2p}\\ 1s_4-2p $	$\begin{array}{r} 0.030-0.034\\ .015018\\ .015019\\ \end{array}$	0.0332 .0160 .0167		
$1s_5 - 2p$.014018	.0156		

If the level $1s_2$ be classified³⁰ as a singlet $({}^{1}P_1)$ and the other levels as components of a triplet $({}^{3}P_{0, 1, 2})$, then it is seen that the specific shift is

²⁹ Using non-orthogonal wave functions, we calculated this to be 0.022 cm⁻¹. This was reported in the Bulletin of the Am. Phys. Soc., Chicago meeting, June, 1933.

³⁰ We may note that the levels $1s_3$ and $1s_5$ should have approximately triplet character, regardless of the coupling, since only the $1s_2$ and $1s_4$ levels perturb each other. Since the $1s_4$ isotope shift is not very different from those for the $1s_3$ and $1s_5$, we believe the above classification is legitimate for our purposes. about 0.017 cm⁻¹ more for the singlet state than for the triplet states. This is in good agreement with the value obtained above from the theory. However, the specific shift for the transitions to the ¹P state is 0.0038 cm⁻¹, theoretically, and 0.0332 cm⁻¹, experimentally.

CONCLUSION

It seems that the theory given in the present paper accounts rather satisfactorily for the observed neon isotope shifts. It predicts that singlets and triplets will have different displacements and the calculated value of the difference agrees well with that which is observed. Further refinement in the wave functions may possibly result in a better value for the specific shift of the singlet (or triplet).

Since, therefore, the neon isotope shifts seem to be due solely to a mass effect, one is led to inquire whether or not this is the general explanation of the isotope shifts found in the light elements. The experiments on zinc⁷ show that the lines due to the isotopes 64, 66, and 68 are equally spaced, so that this may be due to a mass effect, especially since changes in nuclear radius do not seem to have much influence for the lighter nuclei. For copper, Ritschl⁶ finds evidence that the $d^9 s^2 D$ term has an isotope shift of about 0.08 cm⁻¹. If we suppose this to be accounted for by the specific mass effect, then an inspection of the energy expression shows that the absence of a d-electron from the d^{10} shell will have much more effect than the presence of the two s electrons. The argument will not be quite complete, however, until the quantitative results are obtained.