pletely ionic model is not valid for the lithium halides, i.e., their bonds have significant covalent character.

As earlier indicated, the Dunham $-Y_{11}$ reduces to the α_e value when the Morse[15] potential,

$$V(r)=V_D[1-e^{-a(r-r_e)}]^2, \tag{28}$$

is applicable. Table XXI compares the $-Y_{11}$ and α_e values. The comparisons indicate that this compact expression for the potential holds to a good approximation for all the molecules but that it does not provide an exact description for any of them.

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Perturbation Energy Coefficients and Ionization Potentials of the Ground State of Three- to Ten-Electron Isoelectronic Atomic Series*

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The well-known perturbation expansion,

$$E_{nr}^{(N)}(Z)=Z^2\sum_{i=0}^{\infty}\epsilon_i^{(N)}Z^{-i},$$

of the eigenvalues of the nonrelativistic Schrödinger equation for N electrons about a nucleus of charge Z, has been widely used in the past for the extrapolation and interpolation of atomic energies. The presence of many small effects not explicitly taken into account by the perturbation expansion analysis reduce such calculations to a process of empirical curve fitting of limited range and reliability. These small effects include relativistic effects, the mass polarization, and the Lamb terms; to a good approximation, these effect can also be expanded in a descending power series, but with a leading term containing Z^8. On the basis of three plausible assumptions, theoretical approximations make it possible, in a semiempirical fashion, to remove a major portion of these small effects from the experimental data. In this way accurate values for $\epsilon_2^{(N)}$ and good estimates for $\epsilon_3^{(N)}$ have been obtained for $3\leqslant N\leqslant 10$. These coefficients have been used to disclose inaccuracies and to fill gaps in the existing atomic energy data and to estimate electron affinities.

I. INTRODUCTION

Electronic energies of high accuracy for atoms can in theory be obtained by applying the variation principle to a wave function constructed from a large set of suitably chosen basis functions. High accuracy has been obtained only for the He isoelectronic series[1]; more recently, such calculations have been made at a somewhat lower level of accuracy for the Li- and Be-isoelectronic series.[2] Calculations at an equivalent level for a larger number of electrons are not yet available. Further, experimental electronic energies of high accuracy are also not available because, in general, only the first few ionization potentials of a given isoelectronic series have been accurately determined.[3] In this paper a semiempirical scheme is developed, based on conventional perturbation theory, for the accurate extrapolation of total electronic energies or of ionization potentials as a function of the nuclear charge. The scheme is used to disclose inaccuracies, to fill gaps in existing experimental data, and to obtain estimates of the electron affinities. The higher-order perturbation energy coefficients obtained by the analysis are, in themselves of theoretical interest.

For light atoms, the total or experimental energy[4] $E^{(N)}(Z)$ is given to a good approximation by

$$E^{(N)}(Z)=E_{nr}^{(N)}(Z)+E_r^{(N)}(Z), \tag{1}$$

where Z is the nuclear charge and N is the number of electrons. The $E_{nr}^{(N)}(Z)$ and $E_r^{(N)}(Z)$ are the nonrelativistic and the relativistic energies, respectively, which are defined and discussed separately below.

II. NONRELATIVISTIC ENERGY $E_{nr}^{(N)}(Z)$

The nonrelativistic energy $E_{nr}^{(N)}(Z)$ is the eigenvalue of the appropriate nonrelativistic Schrödinger equation. A well-known result of conventional perturbation theory[5] is

$$E_{nr}^{(N)}(Z)=Z^2\sum_{i=0}^{\infty}\epsilon_i^{(N)}Z^{-i}, \tag{2a}$$

where $\epsilon_i^{(N)}$ is the ith-order electronic energy perturba-

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[1] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959).

[2] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

[3] B. Edlén, J. Chem. Phys. **33**, 98 (1960).

[4] Unless otherwise indicated, the data throughout are in atomic units of energy, $2hcR_M=\mu e^4\hbar^{-2}$, where R_M is the Rydberg wave number of the atom or ion in question and μ is the appropriate reduced electronic mass.

[5] See for example, H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35, Part 1, p. 214 and p. 237 ff.

TABLE I. Nonrelativistic ground state electronic energy perturbation coefficients.

N	$-\epsilon_0{}^{(N)\text{a}}$	$\epsilon_1{}^{(N)\text{a}}$	$-\epsilon_2{}^{(N)\text{b}}$	$-\epsilon_3{}^{(N)\text{b}}$
2	1	0.625 000 000 00	0.157 66640[c]	−0.008 6993[c]
3	$1\frac{1}{8}$	1.022 805 212 62	0.4089	0.014
4	$1\frac{2}{8}$	1.559 274 208 40	0.880	0.04
5	$1\frac{3}{8}$	2.327 526 503 21	1.843	0.18
6	$1\frac{4}{8}$	3.258 864 897 51	3.253	0.49
7	$1\frac{5}{8}$	4.353 532 593 16	5.20	1.0
8	$1\frac{6}{8}$	5.661 902 482 47	8.05	1.3
9	$1\frac{7}{8}$	7.134 334 871 78	11.64	2.0
10	2	8.770 829 761 09	16.07	2.9

[a] Obtained from theory.
[b] Obtained from experimental data.
[c] See reference 14.

tion coefficient, a quantity which is independent of Z. The zero- and first-order coefficients, $\epsilon_0{}^{(N)}$ and $\epsilon_1{}^{(N)}$, can be evaluated analytically using the zero-order wave functions, products of hydrogenic functions, and are listed through $N=10$ in Table I.[6] By a slightly different choice of the perturbation term, an alternate expansion of $E_{nr}{}^{(N)}(Z)$ can be obtained in terms of an arbitrary parameter σ, which in general will depend on N:

$$E_{nr}{}^{(N)}(Z)=(Z-\sigma)^2\sum_{i=0}^{\infty}\alpha_i{}^{(N)}(Z-\sigma)^{-i}, \tag{2b}$$

where the $\alpha_i{}^{(N)}$ are new perturbation coefficients. The zero-order wave functions are products of hydrogen-like orbitals, i.e., hydrogenic orbitals in which Z has been replaced by $Z-\sigma$.

In general, the $\alpha_i{}^{(N)}$ are functions of the $\epsilon_j{}^{(N)}$ and σ. The transformation equations relating the $\epsilon_j{}^{(N)}$ and $\alpha_i{}^{(N)}$ can be obtained by expansion of the individual terms of Eq. (2b) and by equating the resulting coefficients of Z with those of like power in Eq. (2a). This yields

$$\epsilon_0{}^{(N)}=\alpha_0{}^{(N)}; \tag{3a}$$

$$\epsilon_1{}^{(N)}=-2\alpha_0{}^{(N)}\sigma+\alpha_1{}^{(N)}; \tag{3b}$$

$$\epsilon_2{}^{(N)}=\alpha_0{}^{(N)}\sigma^2-\alpha_1{}^{(N)}\sigma+\alpha_2{}^{(N)}; \tag{3c}$$

$$\begin{aligned}\epsilon_j{}^{(N)}=\alpha_3{}^{(N)}\sigma^{j-3}&+(j-3)\alpha_4{}^{(N)}\sigma^{j-4}\\&+\frac{1}{2!}(j-3)(j-4)\alpha_5{}^{(N)}\sigma^{j-5}+\cdots+\alpha_j{}^{(N)},\\&\qquad j\geq 3.\end{aligned} \tag{3d}$$

In the discussion that follows, Eq. (2a) is regarded as a special case ($\sigma=0$) of Eq. (2b). The higher-order coefficents in Eqs. (2) can be calculated directly only with great difficulty since they contain infinite summations.[7] It is possible, however, to recover several of these higher-order coefficients from the experimental data, if the data are sufficiently accurate and if the relativistic term $E_r{}^{(N)}(Z)$ can be evaluated.

The first step in the evaluation of these higher-order coefficients is to remove $E_r{}^{(N)}(Z)$ from $E^{(N)}(Z)$ to obtain $E_{nr}{}^{(N)}(Z)$. This is discussed in the following section. Next, assume for generality that the first h coefficients, $\alpha_0{}^{(N)}$ through $\alpha_{h-1}{}^{(N)}$, are known; these known terms are subtracted from $E_{nr}{}^{(N)}(Z)$ to yield the remainder $[E_{nr}{}^{(N)}(Z)]_h$, where

$$[E_{nr}{}^{(N)}(Z,\sigma)]_h=E_{nr}{}^{(N)}(Z)-(Z-\sigma)^2\sum_{i=0}^{h-1}\alpha_i{}^{(N)}(Z-\sigma)^{-i}. \tag{4}$$

Substitution of Eq. (2b) in Eq. (4) yields

$$[E_{nr}{}^{(N)}(Z,\sigma)]_h=(Z-\sigma)^2\sum_{i=h}^{\infty}\alpha_i{}^{(N)}(Z-\sigma)^{-i}. \tag{5}$$

Now, define a difference operator

$$\Delta^p f(Z)=\Delta^{p-1}f(Z+1)-\Delta^{p-1}f(Z), \tag{6}$$

where $f(Z)$ is an arbitrary function of Z, p is a positive integer, and Δ^0 is the identity operator. To recover the leading unknown coefficient $\alpha_h{}^{(N)}$ from $[E_{nr}{}^{(N)}(Z,\sigma)]_h$ for P adjacent pieces of data in a given isoelectronic series, multiply Eq. (5) by $(Z-\sigma)^{p+h-2}$, form the pth difference, and divide by $p!$. This yields

$$(p!)^{-1}\Delta^p\{(Z-\sigma)^{p+h-2}[E_{nr}{}^{(N)}(Z,\sigma)]_h\}=\alpha_h{}^{(N)}+(p!)^{-1}\Delta^p\Big[\sum_{i=1}^{\infty}\alpha_{p+h+i}{}^{(N)}(Z-\sigma)^{-i}\Big], \tag{7}$$

where

$$(p!)^{-1}\Delta^p\Big[\sum_{i=1}^{\infty}\alpha_{p+h+i}{}^{(N)}(Z-\sigma)^{-i}\Big]=(-1)^p\alpha_{p+h+1}{}^{(N)}\prod_{i=0}^{p}(Z-\sigma+i)^{-1}+\cdots. \tag{8}$$

In this manner, $(P-p)$ approximations to $\alpha_h{}^{(N)}$ are obtained. Since $\alpha_0{}^{(N)}$ and $\alpha_1{}^{(N)}$ are known, the first calculations are made for $\alpha_2{}^{(N)}$ using $[E_{nr}{}^{(N)}(Z,\sigma)]_2$ as input data. If the first difference ($p=1$) is taken, $\alpha_2{}^{(N)}$ is contaminated by terms containing $\alpha_4{}^{(N)}$ and higher-order coefficients. If the second difference ($p=2$) is taken, $\alpha_2{}^{(N)}$ is contaminated by terms containing $\alpha_5{}^{(N)}$ and higher-order coefficients, etc. It would thus appear advantageous to reduce the magnitude of the contaminant as far as possible by fixing p at its maximum value of $P-1$. A practical limit to the size of p, however, is determined by the experimental error of the data. If p

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[6] Values of $\epsilon_0{}^{(N)}$ and $\epsilon_1{}^{(N)}$ for $2\leq N\leq 10$ have been recently calculated by D. Layzer, Ann. Phys. (New York) **8**, 271 (1959) and J. Linderberg and H. Shull, J. Mol. Spectroscopy **5**, 1 (1960).

[7] Recently, C. W. Scherr, J. Chem. Phys. **33**, 317 (1960) has made an attempt to compute $\epsilon_2{}^{(2)}$ by such a direct summation while E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956); **109**, 1013 (1958) have obtained a more accurate estimate of this quantity by a perturbation-variation technique. The latter result appears to be the only accurate value of such a higher coefficient in the literature.

is chosen too large, this error is exaggerated so that there occur serious fluctuations among the various values of $\alpha_2^{(N)}$. If sufficient, accurate data are available, the value of p can be selected by the criterion of the minimum root-mean-square deviation from the average value of $\alpha_2^{(N)}$.

After $\alpha_2^{(N)}$ has been obtained for a given p, $(Z-\sigma)^p[E_{nr}^{(N)}(Z,\sigma)]_3$ is formed and differenced $(p-1)$ times to obtain $\alpha_3^{(N)}$. The $\alpha_3^{(N)}$ is also contaminated by $\alpha_{p+h+1}^{(N)}$ and higher-order terms, but the contaminants are of greater magnitude than in the case of $\alpha_2^{(N)}$. The number of $\alpha_i^{(N)}$ which can be determined in this manner is limited only by the quality and quantity of the spectroscopic data and by the quality of the relativistic correction; the accuracy of each successive determination diminishes, however, because of the accumulation of the contaminants. Because only a limited number of expansion coefficients can be recovered from the data, it would be desirable to use that value of σ for which the summation of Eq. (2b) converges most rapidly. The general solution for the optimum value of σ is not available, but the rate of convergence of the first few terms can be discussed. It is shown by direct differentiation[8] of the first two terms of Eq. (2b) that the value of σ which minimizes the *first two* terms of the series, and which is designated as $\sigma^{(N)}$, is given by

$$\sigma^{(N)}=-\epsilon_1^{(N)}/2\epsilon_0^{(N)}. \tag{9}$$

With this condition, $\alpha_1^{(N)}$ vanishes and a variationally bounded upper limit, $\bar{E}_{nr}^{(N)}(Z)$, to the energy is obtained with the first term of Eq. (2b) alone.

This upper limit is given by

$$E_{nr}^{(N)}(Z)<\bar{E}_{nr}^{(N)}(Z)=\alpha_0^{(N)}[Z-\sigma^{(N)}]^2. \tag{10}$$

Substitution of Eqs. (3a) and (9) in Eq. (10) yields

$$\bar{E}_{nr}^{(N)}(Z)=\epsilon_0^{(N)}Z^2+\epsilon_1^{(N)}Z+[\epsilon_1^{(N)}]^2/4\epsilon_0^{(N)}. \tag{11}$$

Further, as may be seen from the transformation equation (3) between the $\epsilon_j^{(N)}$ and $\alpha_i^{(N)}$, the sum of the first three terms of Eq. (2b) equals the sum of the first three terms of Eq. (2a) for all σ, i.e.,

$$\alpha_0^{(N)}(Z-\sigma)^2+\alpha_1^{(N)}(Z-\sigma)+\alpha_2=\epsilon_0^{(N)}Z^2+\epsilon_1^{(N)}Z+\epsilon_2^{(N)}. \tag{12}$$

By comparison of Eq. (11) and Eq. (12) or directly from Eqs. (3c) and (9), the value of $\alpha_2^{(N)}$ corresponding to $\sigma^{(N)}$ is found to be

$$\alpha_2^{(N)}=\epsilon_2^{(N)}-[\epsilon_1^{(N)}]^2/4\epsilon_0^{(N)}. \tag{13}$$

Now for all N, $\epsilon_0^{(N)}<0$ and, hence, $[\epsilon_1^{(N)}]^2/4\epsilon_0^{(N)}<0$ also. In addition, it has been found by an analysis of the data for all isoelectronic sequences investigated $(2\leq N\leq 10)$ that

$$\alpha_2^{(N)}<0, \tag{14}$$

as could be anticipated from second-order perturbation theory. It follows from Eqs. (11), (12), and (14) that the term $[\epsilon_1^{(N)}]^2/4\epsilon_0^{(N)}$ represents the best variational upper bound to $\epsilon_2^{(N)}$ that can be obtained with a single shielding parameter. It further follows from this and from Eq. (13) that the magnitude of $\alpha_2^{(N)}$ has been minimized, so that the maximum rate of convergence towards the sum of the first three terms of Eq. (2b) is obtained in Eq. (10) or Eq. (11).

It is desirable to apply this analysis directly to the ionization potentials since it is these rather than the total electronic energies which are obtained from the experimental spectra. The ionization energies are given by

$$I^{(N)}(Z)=E^{(N-1)}(Z)-E^{(N)}(Z). \tag{15}$$

It follows from Eq. (1) that the ionization energy can be decomposed into a nonrelativistic and relativistic part:

$$I^{(N)}(Z)=I_{nr}^{(N)}+I_r^{(N)}(Z). \tag{16}$$

In view of Eqs. (2a) and (15) it is possible to write

$$I_{nr}^{(N)}(Z)=Z^2\sum_{i=0}^{\infty}e_i^{(N)}Z^{-i}, \tag{17a}$$

where

$$e_i^{(N)}=\epsilon_i^{(N-1)}-\epsilon_i^{(N)}. \tag{18}$$

The $e_0^{(N)}$ and $e_1^{(N)}$ are evaluated theoretically and higher $e_i^{(N)}$ are determined by the differencing procedure outlined above.

In a formally analogous manner to the introduction of an arbitrary parameter in the expression for the nonrelativistic energy, the nonrelativistic portion of the ionization energy can be written as

$$I_{nr}^{(N)}(Z)=(Z-s)^2\sum_{i=0}^{\infty}a_i^{(N)}(Z-s)^{-i}, \tag{17b}$$

where s is an arbitrary parameter and the $a_i^{(N)}$ are functions of the $e_j^{(N)}$ and s. The status of s in Eq. (17b) is ambiguous, and does not have the immediate pictorial (i.e., screening) and theoretical (i.e., modified perturbation term) interpretation that the σ of Eq. (2b) has. The transformation equations relating the $e_i^{(N)}$ and $a_i^{(N)}$ are identical in form to those relating the $\epsilon_i^{(N)}$ and $\alpha_i^{(N)}$, Eq. (3). Let s be chosen as

$$s^{(N)}=-e_1^{(N)}/2e_0^{(N)}. \tag{19}$$

Then, the first two terms of Eq. (17b) are maximized but do not represent a variationally bounded approximation to $I_{nr}^{(N)}(Z)$ as is the case for $E_{nr}^{(N)}(Z)$. Thus, the *a priori* assumption that the choice of Eq. (19) will improve the rate of convergence cannot be made.

III. RELATIVISTIC ENERGY $E_r^{(N)}(Z)$[9]

Assumptions

Under the heading of the relativistic energy $E_r^{(N)}(Z)$ are grouped all the energy terms which are contained in the experimental data exclusive of the nonrelativistic energy. Thus, in addition to the main relativistic effects, there are other smaller terms due to the Lamb shift, mass polarization, etc. Although $|E_{nr}^{(N)}(Z)|\gg|E_r^{(N)}(Z)|$ in the range of Z considered, the removal of the zero- and first-order contributions to

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[8] H. R. Johnson and F. Rohrlich, J. Chem. Phys. **30**, 1608 (1959).

[9] An extended discussion of the material presented in this section is available upon request.

$E_{nr}^{(N)}(Z)$ increases the relative magnitude of $E_r^{(N)}(Z)$ in the remainder sufficiently to interfere with the determination of the higher-order nonrelativistic perturbation-energy contributions. In the test case of the He isoelectronic series, it was found that if no provisions were made for the substantial removal of the relativistic energy, the analysis yields only an order of magnitude estimate of $\alpha_2^{(2)}$ and fails completely in the determination of $\alpha_3^{(2)}$.

A first attempt to deal with the relativistic energy may be based on the following assumptions:

(a) The total relativistic energy of an atomic system with N electrons can be decomposed into N one-electron contributions.

(b) Dirac one-electron theory,[10] combined with the lowest order one-electron radiative correction[11] (Lamb shift) and modified by shielding parameters in the nuclear charge, can be used to describe the relativistic contribution of a single electron with sufficient accuracy.

(c) The relativistic contribution of a closed shell is a constant independent of the number of electrons in outer shells.

For numerical calculations, it is convenient to expand the Dirac energy expression $W(n,k,Z)$ in terms of $(\alpha Z)^2$, where α is the fine-structure constant, The n and k are the Dirac quantum numbers. To insure adequate accuracy in the range $1\leq Z\leq 20$, the expansion has been carried through the fourth order.[12]
Additional accuracy was obtained by including the Lamb shift $\mathcal{E}_{ls}^{(1)}(n,l,Z)$ (or radiative corrections) to order α^3Z^2.

The various perturbation effects due to interaction with the other electrons are approximated in an analogous manner to Sommerfeld's classical treatment of x-ray spectra[13] by replacing Z in the expressions for $W(n,k,Z)$ by $(Z-\rho_n^{(N)})$ in the expressions for $W(n,k,Z)$ and $\mathcal{E}_{ls}^{(1)}(n,l,Z)$. The $\rho_n^{(N)}$ is a relativistic shielding parameter. The relativistic energy, $R_{nkl}(Z,\rho_n^{(N)})$, of a single electron with quantum numbers n, k, and l in an N-electron atomic system is taken to be the sum of the relativistic portion of $W(n,k,Z)$ and the appropriate $\mathcal{E}_{ls}^{(1)}(n,l,Z)$, each with the shielded Z. The total relativistic energy is then

$$E_r^{(N)}(Z)=\sum\nolimits_n \sum\nolimits_k \sum\nolimits_l N_{nkl}R_{nkl}(Z,\rho_n^{(N)}), \qquad (20a)$$

where N_{nkl} is the number of electrons with quantum numbers n, k, and l and the summation extends over all electrons. Because of assumption (c), Eq. (20a) can be written as

$$[E_r^{(N)}(Z)-E_r^{(2)}(Z)]=\sum_{k=1}^{2}\sum_{l=0}^{1} N_{2kl}R_{2kl}(Z,\rho_2^{(N)}) \qquad (20b)$$

for $3\leq N\leq 10$. The $E_r^{(2)}(Z)$ is given approximately by

$$E_r^{(2)}(Z)=\mathcal{E}_r^{(2)}(Z)+\mathcal{E}_{ls}^{(2)}(Z)+\mathcal{E}_m^{(2)}(Z), \qquad (21)$$

where the terms on the right are the relativistic corrections, the Lamb shift corrections, and the mass polarization, respectively. Recently, Pekeris,[1] using an elaborate variational wave function, has computed all three of these effects for He-like ions with nuclear charges of $1\leq Z\leq 10$. By assuming an expansion in powers of Z^{-1}, Scherr and Silverman[14] have recovered the leading expansion coefficients for a perturbation expansion of $\mathcal{E}_r^{(2)}(Z)$, $\mathcal{E}_{ls}^{(2)}(Z)$, and $\mathcal{E}_m^{(2)}(Z)$ from these data by a procedure analogous to that described above for the recovery of the nonrelativistic perturbation coefficients and have thus been able to extrapolate these calculations accurately to the range $11\leq Z\leq 20$.

Test of Assumptions

These assumptions, e.g., as embodied in Eq. (20), can be tested in the case of the helium isoelectronic series. For this series, Dalgarno and Stewart[15] have obtained perturbation series expansions in inverse powers of Z for the terms on the right of Eq. (21). Their expressions may be added to provide a theoretical approximation for $E_r^{(2)}(Z)$:

$$\begin{aligned}&E_r^{(2)}(Z)_{\text{theoret}}\\ &\quad\mathcal{E}_r^{(2)}(Z)+\mathcal{E}_{ls}^{(2)}(Z)+\mathcal{E}_m^{(2)}(Z)\\ &\quad=\alpha^2(A_4'Z^4+A_3'Z^3+A_2'Z^2+A_1'Z+A_0'+\cdots),\end{aligned} \qquad (22)$$

where the A_j''s are known,[9,14] slowly varying functions of Z. The approximate value of $E_r^{(2)}(Z)$ from Eq. (20), to the same order, is simply

$$E_r^{(2)}(Z)_{\text{approx}}=\alpha^2A_4'[Z-\rho_1^{(2)}]^4, \qquad (23)$$

so that this approximation has the same leading term as the theoretical expression, Eq. (22).

A least-squares value of $\rho_1^{(2)}$ may be determined by Eq. (23) by fitting it to Pekeris' values[16] of $E_r^{(2)}(Z)$, $2\leq Z\leq 10$. Expansion of Eq. (23) with this least-squares value of $\rho_1^{(2)}$ yields the least-squares approximations to the coefficients A_3', A_2', etc., for a given value of Z. Thus, for $Z=10$, this procedure gave $A_3'=0.43$, whereas the A_3' of Eq. (22) is 0.46. It is not surprising, then, that

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[10] Reference 5, p. 169.

[11] Reference 5, p. 189, also see J. M. Harriman, Phys. Rev. **101**, 594 (1956).

[12] See, for example, reference 5, p. 173 ff., for a discussion of the relative magnitude of higher-order terms for large values of Z.

[13] A. Sommerfeld, *Atombau und Spektrallinien* (Friedrick Vieweg und Sohn, Braunschweig, 1924), 4th ed., p. 442 ff; and reference 5, p. 174.

[14] C. W. Scherr and J. N. Silverman, J. Chem. Phys. (to be published), have applied the technique described in Sec. II above for the determination of perturbation coefficients to $E_{nr}^{(N)}(Z)$ values obtained from accurate variational wave functions for $N=2$, 3, and 4. The perturbation coefficients so obtained have been used to extrapolate $E_{nr}^{(N)}(Z)$ to larger value of Z. In a similar manner, they have analyzed and extrapolated the relativistic corrections for He-like ions, $E_r^{(2)}(Z)$.

[15] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A247**, 245 (1958).

[16] For $Z=1$, $E_r^{(2)}(1)>0$ and $A_4'(1)<0$.

the values of $E_r^{(2)}(Z)$ obtained from Eq. (23) with the least-squares value of $\rho_1^{(2)}$ are in good agreement for a wide range of Z values with those[14] obtained from Eq. (22).

It is interesting to note that if the Lamb shift is omitted from the left side of Eq. (23) the least-squares value of $\rho_1^{(2)}$ changes by 50% and the root-mean-square deviation increases by a factor of five. This indicates that the Lamb shift, which is ordinarily omitted, should properly be taken into account.

The above constitutes a severe test of the approximation as the relativistic effects are comparatively large for the $n=1$ quantum shell; the relativistic effects due to electrons with quantum number $n>1$ drop off rapidly with increasing n.

Calculation of the $\varrho_n^{(N)}$

The $\rho_n^{(N)}$ have been calculated directly from the experimental data by a procedure based on the work of Sommerfeld[13] in his analysis of the L_{II}–L_{III} splitting in x-ray absorption edges. This analysis, further modified by the addition of the Lamb shift was applied to the $2\,{}^2P_{\frac{1}{2}}-2\,{}^2P_{\frac{3}{2}}$ optical doublet data[17] for the Li-, B-, and F-isoelectronic series for those individual Z values for which such data are available. This procedure furnishes $\rho_2^{(3)}$, $\rho_2^{(5)}$, and $\rho_2^{(9)}$ only. The remaining $\rho_2^{(N)}$ have been obtained by a linear interpolation between these values. Within an isoelectronic series, the $\rho_n^{(N)}$ are slowly varying functions of Z.[18]

The relativistic corrections were then computed using the $\rho_2^{(N)}$ corresponding to the nuclear charge in question. These relativistic corrections are not listed separately but can be obtained by comparison of corresponding entries in Tables V and VI.[9,19] Within the framework of the approximations made, the $\rho_n^{(N)}$ and relativistic corrections obtained in this manner should be fairly reliable as they are based on accurately known small differences between adjacent energy levels.

IV. INPUT DATA AND ERROR ANALYSIS

The experimental ionization potentials used as input data are displayed in Table II. The digits used past those reported by Edlén have not been considered as significant, and are italicized in this table; when properly rounded, all entries will agree exactly with Edlén's revised values.[3] It has been assumed as the basis of the error analysis that each number in Table II may be in error by one unit in the last nonitalicized digit. A rigorous arithmetic consideration of the propagation of this uncertainty has been used to determine the maximum possible uncertainty in each subsequent result. Unless otherwise noted in the tables, all results are rounded such that the uncertainty in the last reported digit is less than 5 units.

TABLE II. Input values of ionization potentials.[a,b,c]

N \ Z	N	$N+1$	$N+2$
3	43.487*14*[d]	146.881*7*[e]	305.93*11*[e]
4	75.192*29*[e]	202.81	386.22
5	66.93	196.659*2*[f]	382.75
6	90.814	238.750*5*[g]	443.00
7	117.22	283.24*4*[e]	505.5
8	109.836*7*[e]	281.94	511.8
9	140.524*5*[e]	330.4	577.8
10	173.931*7*[e]	381.2	646.32

[a] In 10^3 cm^{-1}.

[b] Unless otherwise indicated, these values are from B. Edlén; see footnote 3.

[c] The italicized digits were included in the numerical analysis since they are reported in the literature but were not treated as significant digits in the accompanying error analysis.

[d] K. Lidén and N. Starfelt, Arkiv. Fysik **5**, 127 (1952).

[e] See footnote 17, Vol. I, and the additions and corrections to Vol. I at the ends of Vols. II and III.

[f] S. Glad, Arkiv Fysik **7**, 7 (1954).

[g] K. B. S. Eriksson, Arkiv Fysik **13**, 303 (1958).

V. RESULTS AND DISCUSSION

Perturbation Coefficients

The material presented in the tables is based on Eq. (19). Parallel calculations with $s=0$ were also conducted for comparison but are not presented. The two sets of results are in complete qualitative agreement[20] concerning the second-order coefficients, but the error analysis discussed above indicates that the choice of Eq. (19) is more accurate than the choice $s=0$; in some cases one additional decimal place can be confidently reported. The third-order coefficients obtained via Eq. (19) show the anticipated decrease in magnitude

TABLE III. Ionization energy perturbation coefficients for Eq. (17b).[a,b]

N	$s^{(N)}$[c]	$-a_2^{(N)}$[d]	$a_3^{(N)}$[d]	$-a_4^{(N)}$[d]
3	1.5912209	0.0652*719*	0.023*1699*	0.00*21862*
4	2.1458760	0.104*8156*	0.025*5099*	−0.0*135882*
5	3.0730092	0.216*800*	0.14*4539*	0.06*4617*
6	3.7253536	0.325*5112*	0.30*11526*	0.2*061404*
7	4.3786708	0.44*9842*	0.4*76277*	0.*385753*
8	5.2334796	0.5*765788*	0.3*389898*	0.*0096664*
9	5.8897296	0.74*62025*	0.66*79049*	*0.349706*
10	6.5459796	0.92*20240*	0.92*10168*	0.*494505*

[a] $a_0^{(\text{N})}=\frac{1}{8}$ and $a_1^{(\text{N})}=0$ for $3\leq N\leq 10$.

[b] Only the nonitalicized digits are significant. The italized digits are required to formally reproduce Tables V and VI.

[c] Computed with Eq. (19).

[d] Obtained from experimental data.

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[17] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

[18] It is interesting to note that this procedure is sufficiently sensitive to detect inaccurate experimental or estimated doublet data. Thus, the values of $\rho_2^{(5)}$ for $Z=10$ and $Z=16$ and $\rho_2^{(9)}$ for $Z=16$ determined in this manner from the data in reference 17 are clearly out of line with the smooth trend of the remaining values in these isoelectronic series and have been replaced by interpolated or extrapolated values.

[19] The complete set of screening parameters, $\rho_n^{(N)}$, as well as the relativistic energies, $E_r^{(2)}(Z)$ and $[E_r^{(N)}(Z)-E_r^{(2)}(Z)]$, will be supplied upon request.

[20] Both sets of $\epsilon_i^{(N)}$, e.g., are consistent to the extent that the disagreement is never greater than the uncertainty in the less accurate $s=0$ results. This is an indication that the number of significant figures taken in Table II is not more than warranted.

and vary smoothly with N while those obtained from the choice $s=0$ assume improbably large values in some cases and fluctuate in sign. The greater accuracy of the choice of Eq. (19) might be expected on the basis of the relative magnification of the absolute error of the input data by the factors Z^{p+h-2} and $[Z-s^{(N)}]^{p+h-2}$ called for in the discussion following Eq. (6). The differencing analysis with $p=2$ has been employed to determine the second-, third-, and fourth-order coefficients for each isoelectronic sequence. The theoretical values of $s^{(N)}$, $a_0^{(N)}$ $(a_1^{(N)}=0)$ and the calculated values of $a_2^{(N)}$, $a_3^{(N)}$, and $a_4^{(N)}$ are collected in Table III for $3\leq N\leq 10$. The italicized digits in Table III are all insignificant, and have been retained for the formal bookkeeping purpose of reproducing the input data for Tables V and VI. Table IV tabulates the theoretical values of $e_0^{(N)}$ and $e_1^{(N)}$ and the values of $e_2^{(N)}$, $e_3^{(N)}$, and $e_4^{(N)}$ calculated from the $a_i^{(N)}$ via Eq. (3), appropriately modified. The $\epsilon_2^{(N)}$ and $\epsilon_3^{(N)}$ for $3\leq N\leq 10$ have been computed from the corresponding $e_i^{(N)}$ of Table III via Eq. (18) and are presented in Table I. The accurately known values[14] of $\epsilon_i^{(2)}$, which are also listed in Table I, are required as input in these calculations.

Although there is no theoretical basis at present, it might be anticipated that the order of magnitude of successive perturbation coefficients decreases monotonically. Thus, the point where a given set of semiempirical $\epsilon_i^{(N)}$ has passed from the realm of the semiempiric to that of the wholly empiric is indicated by the point where this anticipated trend is reversed.[21] In the present case, the $\epsilon_4^{(N)}$ derived via Eq. (19) are, in fact, greater in magnitude than the corresponding $\epsilon_3^{(N)}$. They are, however, of the same order of magnitude. The $\epsilon_4^{(N)}$ obtained directly from the choice $s=0$ are so grossly contaminated with higher-order terms that they are an order of magnitude larger than the corresponding $\epsilon_3^{(N)}$ and, in most cases, even greater than the corresponding $\epsilon_2^{(N)}$! This is a further substantiation of the fact, touched on following Eqs. (17b) and (19), and in the above discussion, that, regarded as a numerical technique, the choice of Eq. (19), despite its ambiguous theoretical status, is more effective than the choice $s=0$.

TABLE IV. Ionization energy perturbation coefficients for Eq. (17a).[a]

N	$-e_1^{(N)}$[b]	$e_2^{(N)}$[c]	$e_3^{(N)}$[c]	$e_4^{(N)}$[c]
3	0.397 805 21	0.2512	0.023	0.03
4	0.536 469 00	0.471	0.03	0.07
5	0.768 252 29	0.964	0.14	0.38
6	0.931 338 39	1.409	0.30	0.9
7	1.094 667 7	1.95	0.5	2
8	1.308 369 9	2.85	0.3	2
9	1.472 432 4	3.59	0.7	...
10	1.636 494 9	4.43	0.9	...

[a] $e_0^{(N)}=\frac{1}{8}$ for $3\leq N\leq 10$.
[b] Obtained from theory via Eq. (18).
[c] Obtained from the experimental data of Table III via transformation equations analogous to Eq. (3).

It is of interest to note that there are approximate relationships between the perturbation coefficients and the number of electrons. One such relationship which reproduces the $\epsilon_2^{(N)}$ for $3\leq N\leq 10$ with fair accuracy is

$$\epsilon_2^{(N)}=0.016(N-1)N(N+1). \tag{24}$$

When the first difference of this equation is formed, [cf. Eq. (18)], it yields an expression for $e_2^{(N)}$ which is comparably accurate:

$$e_2^{(N)}=0.048(N-1)N. \tag{25}$$

Ionization Potentials

The $I_{nr}^{(N)}(Z)$ recalculated or extrapolated from the parameters of Table III for $3\leq N\leq 10$ for $(N-1)\leq Z\leq 20$ are collected in Table V. The first column of

TABLE V. Nonrelativistic energies.[a]

Z	$-E_{nr}^{(2)}(Z)$[b]	$I_{nr}^{(3)}(Z)$	$I_{nr}^{(4)}(Z)$	$I_{nr}^{(5)}(Z)$	$I_{nr}^{(6)}(Z)$	$I_{nr}^{(7)}(Z)$	$I_{nr}^{(8)}(Z)$	$I_{nr}^{(9)}(Z)$	$I_{nr}^{(10)}(Z)$	$2R_M$ (cm^{-1})
1	0.527 750 9744									219 355.154
2	2.903 724 375	−0.001								219 444.534
3	7.279 913 341	0.198 1557	0.035							219 457.454
4	13.655 566 17	0.669 2474	0.342 6174	−0.029						219 461.256
5	22.030 971 51	1.393 809	0.924 043	0.304 968	−0.013					219 463.680
6	32.406 246 53	2.369 54	1.759 502	0.895 949	0.413 7947	0.026				219 464.582
7	44.781 445 08	3.595 80	2.8463	1.743 474	1.087 6438	0.534 632	0.002			219 466.018
8	59.156 595 05	5.072 35	4.1838	2.8443	2.017 734	1.291 515	0.501 3955	0.048		219 467.088
9	75.531 712 30	6.799 07	5.7716	4.1969	3.2019	2.304 74	1.286 075	0.641 6122	0.124	219 468.280
10	93.906 806 45	8.775 90	7.6096	5.8006	4.6386	3.573	2.334 08	1.507 38	0.794 4591	219 468.594
11	114.281 8838	11.002 81	9.6977	7.6551	6.3271	5.094	3.639	2.635 46	1.739 62	219 469.379
12	136.656 9483	13.479 77	12.0359	9.7600	8.2666	6.867	5.197	4.021	2.948 514	219 469.597
13	161.032 0030	16.206 77	14.6242	12.1152	10.4569	8.891	7.007	5.660	4.416	219 470.155
14	187.407 0500	19.183 81	17.4625	14.7208	12.8979	11.167	9.068	7.553	6.138	219 470.313
15	215.782 0907	22.410 86	20.5508	17.5765	15.5893	13.693	11.381	9.698	8.114	219 470.730
16	246.157 1264	25.887 94	23.8892	20.6824	18.5310	16.470	13.945	12.094	10.342	219 470.851
17	278.532 1580	29.615 03	27.4776	24.0384	21.7230	19.498	16.759	14.741	12.822	219 471.174
18	312.907 1860	33.592 14	31.3160	27.6445	25.1653	22.776	19.823	17.639	15.554	219 471.605
19	349.282 2112	37.819 25	35.4044	31.5007	28.8577	26.304	23.138	20.788	18.537	219 471.527
20	387.657 2338	42.296 37	39.7429	35.6069	32.8002	30.082	26.703	24.187	21.770	219 471.604

[a] Atomic units.
[b] For $Z\leq 10$ see reference 1 (n^* values); for $Z>10$ see footnote 14.

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[21] A reversal of this nature is observed in the parameters obtained by E. A. Hylleraas and J. Midtdal (*loc. cit.*) in fitting a perturbation expansion series to their theoretical energy values for the He-isoelectronic sequence. In their case,

$$|\epsilon_6^{(2)}|>|\epsilon_5^{(2)}|>|\epsilon_4^{(2)}|.$$

TABLE VI. "Experimental"[a] energies.[b]

Z	$-E^{(2)}(Z)$[c]	$I^{(3)}(Z)$	$I^{(4)}(Z)$	$I^{(5)}(Z)$	$I^{(6)}(Z)$	$I^{(7)}(Z)$	$I^{(8)}(Z)$	$I^{(9)}(Z)$	$I^{(10)}(Z)$
1	0.527 737 09								
2	2.903 784 29	−0.001[d]							
3	7.280 413 23	0.198 1575	0.035[d]						
4	13.657 4437	0.669 2831	0.342 6222	−0.029[d]					
5	22.036 0638	1.393 994	0.924 116	0.304 971	−0.013[d]				
6	32.417 5919	2.370 12	1.759 828	0.896 086	0.413 7980	0.026			
7	44.803 6108	3.597 21	2.8473	1.744 006	1.087 8700	0.534 115	0.002[d]		
8	59.195 9895	5.075 27	4.1859	2.8457	2.018 526	1.290 599	0.500 4700	0.048	
9	75.596 915	6.80444	5.7756	4.1998	3.2038	2.303 29	1.284 650	0.640 2953	0.123
10	94.008 884	8.785 01[d]	7.6168[d]	5.8060	4.6425	3.571	2.332 00	1.505 45	0.792 5129
11	114.434 730	11.017 43	9.7094	7.6642	6.3340	5.091	3.636	2.632 71	1.736 92
12	136.877 605	13.502 14	12.0540	9.7743	8.2782	6.863	5.193	4.017	2.944 918
13	161.340 998	16.239 55	14.6510	12.1369	10.4752	8.887	7.002	5.656	4.411
14	187.828 720	19.230 32	17.5008	14.7523	12.9252	11.162	9.063	7.548	6.132
15	216.344 93	22.474 87	20.6043	17.6207	15.6286	13.688	11.375	9.691	8.107
16	246.894 09	25.974 03	23.9615[d]	20.7432[d]	18.5859[d]	16.464	13.938	12.087	10.335
17	279.481 05	29.728 42[d]	27.5736[d]	24.1199[d]	21.7977[d]	19.491[d]	16.752	14.734	12.814
18	314.110 94	33.738 85[d]	31.4412[d]	27.7516[d]	25.2645[d]	22.769[d]	19.817[d]	17.631[d]	15.545[d]
19	350.789 27	38.006 13[d]	35.5649[d]	31.6392[d]	28.9871[d]	26.298[d]	23.132[d]	20.780[d]	18.528[d]
20	389.521 86	42.531 16[d]	39.9458[d]	35.7832[d]	32.9662[d]	30.077[d]	26.698[d]	24.180[d]	21.762[d]
Maximum deviation from data in Moore[e]		0.0044 for $Z=14$	−0.0071 for $Z=15$	0.0023 for $Z=12$	−0.032 for $Z=15$	−0.033 for $Z=16$	−0.016 for $Z=17$	−0.012 for $Z=15$	−0.011 for $Z=17$

[a] Nonrelativistic plus relativistic energies.

[b] To convert to cm^{-1}, multiply by $2R_M$; to convert to eV, multiply by $(hc/\text{eV})2R_M=(1.23977\times10^{-4})2R_M$.

[c] For $Z\leq 10$ see reference 1 (n^* values); for $Z<10$ see footnote 14.

[d] No experimental data available.

[e] These entries give an indication of the magnitude of the inaccuracies of the values quoted by Moore for larger values of Z.

Table V also lists the values of the nonrelativistic energy of He-like ions, $E_{rn}^{(2)}(Z)$, for $1\leq Z\leq 20$ as obtained by a perturbation extrapolation[14] of Pekeris' highly accurate variational data.[1] Thus, to obtain the value of $E_{nr}^{(N)}(Z)$ for any atom or ion in this range from Table V, it is merely necessary to add the appropriate $E_{nr}^{(2)}(Z)$ and $I_{nr}^{(N)}(Z)$ from left to right. In Table VI, which has a similar format to Table V, the relativistic corrections have been added to the entries so that the "experimental" energies are listed. In the last column of Table V are also listed the Rydberg factors, $2R_M$, for convenience in converting from a.u. to cm^{-1} or to eV. The ionization potentials listed in Tables V and VI are all reported to one additional, otherwise unwarranted, digit in order to minimize round-off error when summing horizontally to obtain total electronic energies.[22] The number of digits actually warranted for each entry, with the exception of the first four entries in each column (negative ions, discussed below, and the input data), is the number of significant *decimal places* in the corresponding $\alpha_2^{(N)}$. The energies in Tables V and VI are in atomic units[4] which are the appropriate units to permit direct comparison of experimental data with variational energy calculations. In addition to the extrapolations to Z equals 20, the gaps in the experimental data for Z equals 10 are also filled. These estimates should be more reliable than previous estimates[23] as the first two terms in the extrapolation formula have been given their theoretical values and the relativistic effects have been taken into account. For the same reason, all of the extrapolated values in Table VI, i.e., all entries for $Z\geq N+3$, should be more accurate than the corresponding values in the literature,[17] which, for the most part, are actually based on empirical extrapolations.[3]

TABLE VII. Some electron affinity values.[a]

Ion	J. R.[b]	Edlén[c]	Present paper[d]	Exp.[e]
He^- $^2S_{\frac{1}{2}}$	···	0.19	−0.02	>0
Li^- $^1S_0$	···	0.82	0.95	>0
Be^- $^2P_{\frac{1}{2}}$	···	−0.19	−0.78	<0
B^- $^3P_0$	0.75	0.33	−0.36	>0
C^- $^4S_{\frac{3}{2}}$	1.10	1.24	0.69	1.25
N^- $^3P_2$	0.49	0.05	0.06	>0
O^- $^2P_{\frac{3}{2}}$	1.34	1.49	1.30	1.465
F^- $^1S_0$	3.29	3.50	3.34	3.52

[a] In electron volts.

[b] Reference 8. For comparison, their arbitrary multiplicative factor of 1.1 has been divided out.

[c] Reference 3. His O^- value seems to be a misprint and is corrected here.

[d] Arbitrarily presented to two decimal places. These numbers may be too low by roughly as much as one electron volt.

[e] L. M. Branscomb, private communication.

Electron Affinities

The electron affinities of the neutral atoms are obtained by extrapolation with the $s^{(N)}$ and $a_j^{(N)}$ of Table III. The results are listed in Table VII, together

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[22] From the assumption of 1 unit of possible error for the entries in Table II, it follows that the corresponding entries of Tables V and VI, due to the additional digit carried and to the conversion factor to atomic units, have 46 units of possible error in the last decimal place reported.

[23] This should probably be true also of a non-isoelectronic extrapolation procedure, such as W. Finkelnburg and F. Stern, Phys. Rev. **77**, 303 (1950); also see W. Finkelnburg and W. Humbach, Naturwiss. **42**, 35 (1955).

with the results of some previous investigators. Estimates of the uncertainty for $N=3$, 4, and even 5 are very difficult to make, as $(Z-s^{(N)})$ in these cases is less than unity. For the higher N, the values may be as much as 1 eV too low because of the large, negative, inaccurate $\alpha_4^{(N)}$ values.[24] The perturbation procedure is quite unsuited for the investigation of negative ions, so it is unfortunate, as Edlén remarks,[3] that probably the only practicable extrapolation procedure in this connection is an isoelectronic one.

The data of Johnson and Rohrlich, when account is taken of their *ad hoc* multiplicative factor, and the data of Edlén both fall within the limits set above, as they must, since the present method of estimation furnishes the maximum information permitted from the available ionization energies.

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[24] The situation is aggravated by the fact that summing the perturbation series through fourth order resulted, for all N, in a further arithmetic loss of significant figures due to the positive and negative terms nearly cancelling.

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Effect of Matrix Interactions and Buffer Gases on the Atomic Nitrogen Hyperfine Splitting*†

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Electron spin resonance studies of trapped nitrogen atoms show that the matrix interaction increases the hyperfine splitting by some 10 to 20% of the free atom value of 10.45 Mc/sec. A similar increase in the hyperfine splitting is produced by buffer gases used in optical spin-polarization studies of nitrogen atoms. These effects can be accounted for by van der Waals interactions between the trapped atom and the matrix or buffer gas particles. These interactions introduce $(2s)(2p)^4$ excited states into the nitrogen wave function. Since the $2p$ shell of the ^4S nitrogen atom already contains three electrons with the same spin, only that $2s$ electron with opposite spin can be excited. This increases the unpaired electron density at the nucleus. An approximate calculation of this effect, carried out using perturbation theory, is in qualitative agreement with the experimental results. The magnitude of the effect is proportional to the polarizability of the matrix or buffer gas particle, so that the hyperfine splitting increases with the size of the perturbing species.

INTRODUCTION

ELECTRON spin resonance (ESR) studies of nitrogen atoms trapped at liquid helium temperature in inert gas matrices[1,2] have shown that the interaction of the nitrogen atom with its surroundings increases the nitrogen hyperfine splitting (hfs) constant by some 10 to 20% of the free atom value of 10.45 Mc/sec.[3] More recently, a spin-exchange optical polarization method has been used to determine the pressure shifts of the nitrogen hyperfine splitting in various buffer gases.[4] The results of these two experiments are in qualitative agreement.

Effects of this type have been observed previously for hydrogen atoms and for alkali atoms in both inert solids[5,6] and in the gas phase.[7] The matrix and pressure shifts in nitrogen are, however, somewhat different from the shifts found for hydrogen and the alkali atoms, as might be expected from the difference in atomic structure between the two types of atoms. Specifically, the matrix and pressure shifts always increase the nitrogen hyperfine splitting, while the hydrogen and alkali atom shifts are sometimes positive and sometimes negative.

In this paper we shall make an approximate calculation of the matrix and pressure shifts of the nitrogen hyperfine splitting following an earlier treatment of the hydrogen atom.[8] In the hydrogen atom the matrix perturbation was assumed to be a combination of van der Waals and exchange forces. It was found that the

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