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Hyperfine Pressure Shift and van der Waals Interaction. II. Nitrogen-Helium System*

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In continuation of a series of investigations of hyperfine pressure shifts (HPS) in interacting atoms, an investigation of the long-range interaction of nitrogen atoms in a helium atmosphere is reported. The procedure requires wave functions perturbed to first order in the van der Waals and nuclear hyperfine Hamiltonians, respectively. The van der Waals perturbed wave function is obtained through a variational procedure described previously for the H-He system. The first-order hyperfine wave function is a moment-perturbed (MP) function used in an earlier study of the short-range N-He interaction. The theoretical result for the long-range contribution to HPS is 0.22 cps/mm Hg to be combined with a contribution from short-range of 0.91 cps/mm Hg, as compared with a total experimental HPS of 0.27±0.07 cps/mm Hg. Various factors which might contribute to the difference between theory and experiment are discussed. In particular, the role of correlation at short range is stressed.

I. INTRODUCTION

The present work is a continuation of efforts to arrive at a quantitative understanding of the origin of hyperfine pressure shifts (HPS) of atoms in buffer gas atmospheres.[1] The pressure shift for nitrogen atom has been studied experimentally through the optical pumping technique[2] in a number of rare gases. In our present investigation we have singled out the N-He system for detailed study. In an earlier paper[3] we have analyzed the contribution from short-range effects for this system, arising from an interplay of the overlap effect between the two atoms and the exchange polarization within the nitrogen atom. In the present work we are concerned with long-range effects. For this purpose, we utilize a variational method applied previously to study the van der Waals (VDW) distortion in H-He system.[4] This work will be referred to hereafter as I.

Calculation of the long-range contribution to HPS requires[4, 5] a knowledge of the third-order energy which consists of two orders in the VDW interaction and one order in the hyperfine effect. We have calculated this energy using the first-order perturbed wave function due to the VDW effect obtained variationally and the first-order wave function due to the action of the nuclear moment determined by the moment-perturbation (MP) procedure.[6] This method eliminates the need for using conventional perturbation theory with associated uncertainties for the excited states.[5] It should be noted here that an equivalent procedure would have been to consider the wave function perturbed to second order in the VDW interaction only. In the present case, it is felt that there was likelihood of more error in a second-order wave function calculation than in the procedure utilized here involving two first-order calculations.

Section II deals with variational calculations for the VDW energy and wave functions. In Sec. III, the procedure for the hyperfine shift calculation will be described. In Sec. IV, we describe the statistical averaging procedure to evaluate the long-range contribution to the HPS, which is then combined with previously calculated short-range HPS and compared with experiment. An analysis of the possible sources of discrepancy between theory and experiment is made and possible avenues for future investigations are indicated.

II. LONG-RANGE VAN DER WAALS CALCULATION

In I, we have described a variational technique for treating the long-range van der Waals interaction between two neutral atoms. The system considered there was H-He. However, as indicated in I, the approach was developed with the intention that it should be applicable to larger systems. The present paper deals with the extension of that procedure to the interaction between nitrogen and helium atoms. The variation function used represents a compromise between maximum flexibility in terms of variational parameters and practicability in terms of the computational aspects.

The N-He variational wave function is expressed in the form

$$\delta\Psi = f\Psi_0, \tag{1}$$

where Ψ_0 is the unperturbed wave function. For this function we have used the product of the Hartree-Fock determinants for the two isolated atoms, the radial functions being those given by Clement.[7] The form of the perturbation function is determined from a consideration of the interaction Hamiltonian for this system:

$$\mathcal{H}' = \frac{Z_{\mathrm{He}} Z_{\mathrm{N}}}{R} - \sum_{i=1}^{2} \frac{Z_{\mathrm{N}}}{r_{i\mathrm{N}}} - \sum_{i=3}^{9} \frac{Z_{\mathrm{He}}}{r_{j\mathrm{He}}} + \sum_{i=1}^{2} \sum_{j=3}^{9} \frac{1}{r_{ij}}\,, \tag{2}$$

where $i = 1, 2$ and $j = 3, \ldots 9$, refer to electrons of the helium and nitrogen atoms, respectively, and we have used atomic units here and throughout the rest of the paper. In the van der Waals region, the Hamiltonian (2) can be expressed in terms of spherical harmonics. We consider here only the dipole-dipole interaction term of the expansion which has the form

$$\mathcal{H}' = \frac{1}{R^3} \sum_{i=1}^{2} \sum_{j=3}^{9} \sum_{m=-1}^{1} C_m r_i r_j Y_1^{m*}(\Omega_i) Y_1^{m}(\Omega_j), \tag{3}$$

where $C_m = (4\pi/3)(\delta_{|m|,1} - 2\delta_{m,0})$.

The function f is taken as

$$f = \frac{1}{R^3} \sum_{m=-1}^{1} \sum_{n,k=1}^{N_0} C_m A_{nk} \sum_{i=1}^{2} \sum_{j=3}^{9} r_i^{\,n} r_j^{\,k} Y_1^{m*}(\Omega_i) Y_1^{m}(\Omega_j). \tag{4}$$

As in I, we have obtained the optimum values of the parameters A_{nk} by a variation perturbation technique. This requires the minimization of the functional

$$J(\delta\Psi) = \langle \delta\Psi | \mathcal{H}_0 - E_0 | \delta\Psi \rangle + 2 \langle \delta\Psi | \mathcal{H}' | \Psi_0 \rangle, \tag{5}$$

where $\mathcal{H}_0$ and E_0 are the Hamiltonian and total energy of the N-He system at infinite separation. The approach followed for N-He is exactly analogous to that described in I. As shown there, the function $J(\delta\Psi)$ will contain terms involving the difference between the actual Hamiltonian and the Hartree-Fock Hamiltonian. These terms represent the effect of intra-atomic correlation on the perturbed wave function. It was shown in the case of H-He that this effect represents a change of only 3% in th energy. It does not necessarily follow that the effect of these intra-atomic correlation terms in the nitrogen-helium system will also be quite as small. However, in view of the great cost in terms of computational complexity of keeping these terms, we have neglected this effect. Thus, in this case, the functional consists of three integrals:

$$J(\delta\Psi) = \tfrac{1}{2} \left\langle \Psi_0 \left| \sum_{i=1}^{9} \left| \frac{\partial f}{\partial r_i} \right|^2 \right| \Psi_0 \right\rangle + \left\langle \Psi_0 f \left| \sum_{i=1}^{9} \frac{[L_i^{\,2}, f]}{2 r_i^{\,2}} \right| \Psi_0 \right\rangle + 2 \langle \Psi_0 f | \mathcal{H}' | \Psi_0 \rangle\,. \tag{6}$$

The expression for $J(\delta\Psi)$ may be re-expressed in terms of radial integrals as

$$J(\delta\Psi) = \frac{4}{9R^6} \sum_{n,k,n',k'=1}^{N_0} A_{nk}A_{n'k'} \{(nn'+2)I(\mathrm{He},\mathrm{He};n+n'-2)[2I(1s1s;k+k')$$
$$+2I(2s2s;k+k')+3I(2p2p;k+k')-2I(1s2p;k)I(1s2p;k')-2I(2s2p;k)I(2s2p;k')]$$
$$+(kk'+2)I(\mathrm{He},\mathrm{He};n+n')[2I(1s1s;k+k'-2)+2I(2s2s;k+k'-2)+3I(2p2p;k+k'-2)]\{$$
$$+\frac{16}{9R^6}\sum_{n,k=1}^{N_0} A_{nk} I(\mathrm{He},\mathrm{He};n+1)[2I(1s,1s;k+1)+2I(2s,2s;k+1)$$
$$+3I(2p,2p;k+1)-2I(1s2p;1)I(1s2p;k)-2I(2s2p;1)I(2s2p;k)], \tag{7}$$

where the integrals $I(ij;n)$ are defined in the same manner as in I, namely,

$$I(ij;n) = \int_0^\infty P_i(r) r^n P_j(r) dr. \tag{8}$$

Minimizing the functional (7) results in a system of linear equations which are then solved for the variation parameters A_{nk}. The dipole-dipole van der Waals energy is then obtained by substituting back the values of these parameters in the function (7). This energy is expressed in the form

$$E_{\mathrm{VDW}} = C_{dd}/R^6. \tag{9}$$

The results of this calculation are given in Table I for various numbers of variation parameters. With the computer facilities available (IBM 7040), 49 parameters was the maximum number that was practicable. However, we see from Table I that the convergence is quite good with 49 parameters. If the intra-atomic correlation terms had been included, the number of parameters would have to be reduced since the computer time would increase substantially.

III. LONG-RANGE HYPERFINE EFFECT

In calculating the HPS for N-He, we must obtain the hyperfine energy for the van der Waals perturbed wave function. Because of the form of the van der Waals interaction Hamiltonian, the lowest-order energy contribution will involve second order in this operator. The calculation of hyperfine energy may be considered as a problem in double perturbation theory. If the perturbation Hamiltonian is written as

$$\mathcal{H}' = \mathcal{H}'_{\mathrm{VDW}} + \mathcal{H}'_{\mathrm{hfs}}, \tag{10}$$

where $\mathcal{H}'_{\mathrm{hfs}} = A_c \vec{I} \cdot \sum_i \vec{s}_i \delta(\vec{r}_i)$, (11)

with $A_c = (16\pi/3)(\mu_N/I)\mu_0 a_0^{-3}$, (12)

μ_N and I being the nuclear moment and spin, and μ_0 the Bohr magneton, $\delta(\vec{r}_i)$ being expressed in atomic units. Then the energy which is required will be $\delta^3 E_{1,2}$ where the first subscript gives the order in $\mathcal{H}'_{\mathrm{hfs}}$ while the second refers to $\mathcal{H}'_{\mathrm{VDW}}$. From the analysis of I with

$$\delta E_{\mathrm{VDW}} = 0, \tag{13}$$

$$\langle \Psi_0 | \delta\Psi_{\mathrm{VDW}} \rangle = 0, \tag{14}$$

$$\langle \Psi_0 | \delta\Psi_{\mathrm{hfs}} \rangle = 0, \tag{15}$$

the expression for $\delta^3 E_{1,2}$ is given by

$$\delta^3 E_{12} = 2\langle \delta\Psi_{\mathrm{VDW}} | \mathcal{H}'_{\mathrm{VDW}} | \delta\Psi_{\mathrm{hfs}} \rangle + \langle \delta\Psi_{\mathrm{VDW}} | \mathcal{H}'_{\mathrm{hfs}} | \delta\Psi_{\mathrm{VDW}} \rangle - \delta E_{\mathrm{hfs}} \langle \delta\Psi_{\mathrm{VDW}} | \delta\Psi_{\mathrm{VDW}} \rangle. \tag{16}$$

In this expression, $\delta\Psi_{\mathrm{VDW}}$ is the perturbed wave function obtained in Sec. II and $\delta\Psi_{\mathrm{hfs}}$ is the moment-perturbed (MP) wave function presented in an earlier paper.[3] The hyperfine energy δE_{hfs} is given by

$$\delta E_{\mathrm{hfs}} = \langle \Psi_0 | \mathcal{H}'_{\mathrm{hfs}} | \Psi_0 \rangle, \tag{17}$$

and is zero for Ψ_0 as chosen in Sec. II. When an unrestricted Hartree-Fock approximation is used[3,8] for the nitrogen atom, $\delta E_{\rm hfs}$ is nonvanishing and leads to a finite observed hyperfine constant. We shall use for $\delta E_{\rm hfs}$ the value corresponding to the experimental[2] hyperfine constant 10.45 Mc/sec for isolated nitrogen atoms.

It should be noted here that the three terms included in our Eq. (16) correspond in form to the terms in a similar energy expression given by Adrian[5] in his HPS calculation using conventional perturbation theory. Substituting expressions given previously for the quantities which appear in Eq. (16), we can express $\delta^3 E_{12}$ in terms of radial integrals. The resulting expressions for the three terms are

$$\begin{aligned}\langle \delta\Psi_{\rm VDW} | \mathcal{H}'_{\rm VDW} | \delta\Psi_{\rm hfs}\rangle = \frac{8}{9R^6} A_c \sum_{n,k=1}^{N_0} A_{nk} I(\mathrm{HeHe}; n+1)\{&-I(\delta 1s2p; 1)\, I(2p1s, k) - I(\delta 2s2p; 1) I(2p2s; k) \\ &- I(\delta_{1s2p}; k) I(2p1s; 1) - (\delta_{2s2p}; k) I(2p2s; 1) + I(2s2p; 1) I(2p1s; k) \\ &+ I(2s2p; k) I(2p1s; 1)[I(\delta 1s2s; 0) + I(\delta 2s1s; 0)]\},\end{aligned} \tag{18}$$

$$\begin{aligned}\langle \delta\Psi_{\rm VDW} | \mathcal{H}'_{\rm hfs} | \delta\Psi_{\rm VDW}\rangle = \frac{4}{9R^6} A_c \sum_{n,k,n'k'=1}^{N_0} A_{nk} A_{n'k'} I(\mathrm{HeHe}; n+n')[&4\chi_{1s}(0)\chi_{2s}(0) I(1s2p; k) I(2p2s; k') \\ &+ \chi_{1s}{}^2(0) I(1s2p; k) I(2p1s; k') + \chi_{2s}{}^2(0) I(2s2p; k) I(2p2s; k')],\end{aligned} \tag{19}$$

$$\begin{aligned}\langle \delta\Psi_{\rm VDW} | \delta\Psi_{\rm VDW}\rangle = \frac{8}{9R^6} \sum_{n,k,n'k'=1}^{N_0} A_{nk} A_{n'k'} I(\mathrm{HeHe}; n+n') \\ \times [-I(1s2p; k) I(2p1s; k') - I(2s2p; k) I(2p2s; k')],\end{aligned} \tag{20}$$

where the notation for the radial integrals is as in (8).

Using our 49-term variation function for $\delta\Psi_{\rm VDW}$, the results for the three terms are

$$2\langle \delta\Psi_{\rm VDW} | \mathcal{H}'_{\rm VDW} | \delta\Psi_{\rm hfs}\rangle = (3574.5/R^6)\ \mathrm{Mc/sec}, \tag{21}$$

$$\langle \delta\Psi_{\rm VDW} | \mathcal{H}'_{\rm hfs} | \delta\Psi_{\rm VDW}\rangle = (48.2/R^6)\ \mathrm{Mc/sec}, \tag{22}$$

$$\delta E_{\rm hfs} \langle \delta\Psi_{\rm VDW} | \delta\Psi_{\rm VDW}\rangle = (4.0/R^6)\ \mathrm{Mc/sec}. \tag{23}$$

The magnitudes of the three terms are in the same relative order as predicted earlier by Adrian.[5] As previously indicated, the third term would be zero if core-polarization effects were neglected and is seen to be still negligible when one includes such effects through the experimental value for $\delta E_{\rm hfs}$. Our ratio between the second and first terms is somewhat smaller than that obtained by Adrian through his semiquantitative estimates.

The change $\Delta a_{\rm N}(R)$ in the hyperfine constant as a function of R can be obtained using the relation

$$\Delta a_{\rm N}(R) = \delta^3 E_{12}/IJ, \tag{24}$$

where $I = 1$ and $J = \frac{3}{2}$ for the N^{14} atom.

HYPERFINE PRESSURE SHIFT AND DISCUSSION

Having obtained the change in the hyperfine constant $\Delta a_{\rm N}(R)$ as a function of interatomic separation, we can caluclate the hyperfine pressure shift (HPS) for the system by averaging $\Delta a_{\rm N}(R)$ over all values of R. As shown by Clarke[9] and as discussed in I, it is entirely sufficient to carry out a classical statistical average in this case. In the Boltzmann weight factor, $R^2 \exp[-V(R)/kT]$, we have used the Lennard-Jones potential[10]

$$V(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6]. \tag{25}$$

The parameters σ and ϵ are determined empirically following a procedure described by Adrian.[5] Thus, σ was taken as the mean of the collision radii of helium and nitrogen atoms. These were determined from virial coefficients for helium and empirical rules due to Pauling in the case of nitrogen.[11] The quantity ϵ was determined by equating the R^{-6} term in (25) to our dipole-dipole energy term calculated in Sec. II. The value of ϵ and σ thus obtained are

$$\epsilon/k = 15.7\,^\circ\mathrm{K}, \quad \sigma = 5.35 a_0, \tag{26}$$

as compared to the values

$$\epsilon/k = 26.7\,^\circ\mathrm{K}, \quad \sigma = 5.35 a_0, \tag{27}$$

TABLE I. Coefficients in the van der Waals energy expansion (atomic units).

Number of variation parameters	C_{dd}
4	-4.2614
9	-4.3297
16	-4.3487
25	-4.3592
36	-4.3652
49	-4.3678

obtained by Adrian[5] using an estimated dipole-dipole potential. The final expression for the HPS is given by:

$$a_P=\frac{\partial}{\partial P}(\langle \Delta a_{\mathrm{N}}(R)\rangle)$$
$$=\frac{1}{kT}\int \Delta a_{\mathrm{N}}(R)e^{-V(R)/kT}d\tau_R. \qquad (28)$$

For purposes of further discussion, we have plotted $\Delta a_{\mathrm{N}}(R)$ and $R^2\exp[-V(R)/kT]$ against R in Fig. 1. As discussed in I for H-He, carrying out this average brings up the question of specifically what range of interatomic distance may be termed "long range". It is clear that the van der Waals calculation described above may be applied only at values of R greater than some minimum distance. The multipole expansion for the interaction Hamiltonian is only valid for large separations. The best procedure for bridging the gap between large and small R is to carry out a variational calculation in the intermediate region where both exchange and polarization effects are important. Such a calculation would be similar to a molecular calculation and is beyond the scope of the present work. An alternative approach is to apply a cut-off process as discussed in I. The justification for the cut-off procedure is that the polarization effect should not diverge at small R as in Fig. 1 but should instead decrease continuously in magnitude below a certain value of R and join the short-range curve. A plausible choice of R_C was made in I from considerations of the convergence of the series in R^{-n} in the long-range energy and hyperfine constant expressions. Since we have not calculated higher multipole contributions for the N-He system, we cannot utilize the same considerations as in I. Instead we have used the form of the empirical potential in Eq. (25) for arriving at a choice for R. The zero of the empirical potential occurs at $R_0=5.35$ and minimum at $R_0=5.5$. Either of these points could be considered as plausible choices for R_C. However, our long-range polarization calculation of the spin density may not be valid for these values of R and so we have chosen a slightly larger distance $R_C=6.5$ as a reasonable cut-off distance. The sensitivity of the pressure shift to the choice of R_C can be gauged from Table II where results are listed for a number of values of R_C. For our choice of $R_C=6.5$, the long-range pressure shift is given by

$$(a_p)_{\mathrm{LR}}=0.22\ \mathrm{cps/mm\,Hg}. \qquad (29)$$

This value is to be compared with earlier values of 0.76 cps/mm Hg and 0.26 cps/mm Hg obtained by Adrian.[5,12] The first of these values was an estimate obtained from conventional perturbation theory with the usual approximations regarding energy denominators. The second result was briefly stated to have been derived from a variational calculation. It is, however, difficult to make any comparison between this latter result and ours, since no details of the variational calculation employed[12] are available and presumably no cut-off procedure was utilized in the statistical averaging. From the results in Table II, it appears that one can make a significant overestimate of pressure shift if no cut-off is used.

The long-range contribution in Eq. (26) is to be combined with the short-range contribution calculated in an earlier paper.[3] This result utilized the parameters (27) proposed by Adrian[5] for the potential $V(R)$ in (25). On utilizing the parameters in (26) derived from our dipole-dipole energy, the short-range contribution has the value

$$(a_p)_{\mathrm{SR}}=0.91\ \mathrm{cps/mm\,Hg}. \qquad (30)$$

The short-range contribution thus appears to be a factor of 4 larger than the long-range effect. The exact ratio is not, of course, very meaningful be-

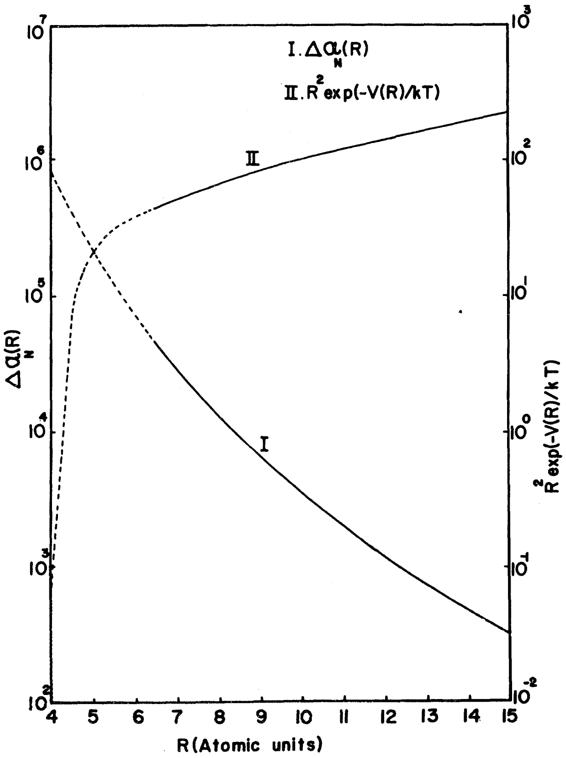

FIG. 1. Frequency shift $\Delta a_N(R)$ in cps and the Boltzmann weighting factor $R^2\exp[-V(R)/kT]$ in units of a_0^2.

TABLE II. Dependence of $(a_p)_{\mathrm{LR}}$ on cutoff.[a]

R_c [a]	$(a_p)_{\mathrm{LR}}$ (cps/mm Hg)
4.0	0.712 678
4.5	0.653 808
5.0	0.459 800
5.5	0.380 127
6.0	0.264 746
6.5	0.223 173
7.0	0.162 061
7.5	0.139 092
8.0	0.103 850

[a] The range of R in the averaging process is $R_c \to \infty$.

cause of the arbitrariness in the choice of R_c. However, one can state definitely that within the approximations utilized in these calculations, the short-range and long-range results are of the same order of magnitude. For larger, more polarizable, buffer-gas atoms, one can, however, expect the van der Waals effect to increase and possibly dominate the short-range effect.

Combining the calculated values of $(a_p)_{\text{LR}}$ and $(a_p)_{\text{SR}}$, our theoretical value of the (HPS) for the N-He system is

$$(a_p)_{\text{theo}} = 1.13 \text{ cps/mm Hg},$$

which is to be compared with the experimental value[2] of 0.27 ± 0.07 cps/mm Hg. The theoretical result is well outside the quoted value of 25% for the experimental error range. In view of this, it would be helpful to have confirmation of the experimental value by a remeasurement, hopefully with a smaller limit of error. However, at the present time it does appear that the predominant change will have to be in the theoretical result in order to obtain agreement with experiment. It is, therefore, worthwhile to consider here some areas in which the theoretical procedure could be improved and their possible relative impact on the HPS result.

First of all, we analyze the calculation of $\Delta a(R)_{\text{LR}}$. The variational procedure we have adopted here has been quite successful in predicting van der Waals energy curves in other systems,[4,13] and in the present case has shown good convergence. A somewhat different variational function adapted particularly to analytic one-electron wave functions[7] has recently been utilized in energy calculations[14] without substantial improvement. While the VDW polarization is an interatomic correlation effect, it can be significantly dependent on intra-atomic correlation within the nitrogen atom. This latter type of correlation has not been included in the present calculation. This intra-atomic correlation was not found to be very important in the H-He system, but its importance with respect to the N-He system would have to be assessed through an actual calculation. Another source of uncertainty in the long-range calculation of HPS is the determination of a cut-off distance R_c. The long-range HPS is quite sensitive to the choice of R_c, and as mentioned earlier, a molecular-type calculation for the intermediate region would eliminate the need for selecting a cut-off distance. However, even if all of these effects were included in the calculation of $(a_p)_{\text{LR}}$, it is extremely doubtful that the result could become negative as would be required in order to counteract the large short-range contribution. In fact, it is our feeling that the result for $\Delta a(R)_{\text{LR}}$ as given in Fig. 1 would not be changed significantly by inclusion of correlation effects.

Thus attention must be focused on possible improvements in the short-range calculation. In looking for sources that could significantly alter the theoretical result for the short-range effect to improve agreement with experiment, two factors suggest themselves for consideration. First, the distortion of the atomic orbitals that could arise from the interatomic potential have been neglected. It is conceivable, but not very likely, that this type of distortion could significantly counteract the effects of the calculated Pauli distortion. Possibly a more important source that could influence the short-range result significantly is the correlation effect, both among orbitals within the atom and between orbitals on the two different atoms. An analysis of the effects of correlation on HPS would thus be very useful; however, such a calculation for the N-He system would be rather complicated. The relatively simple H-He system would serve as a more reasonable starting point in a consideration of correlation effects on HPS, in view of the fact that a similar situation arises in that system.[15]

In conclusion, we would like to emphasize that the procedure employed in these calculations has special merit in that it allows an evaluation of HPS from first principles without the introduction of any arbitrary parameters. The utilization of the MP procedure is somewhat novel for this problem and makes it easily extendable to more complicated systems. It would be illuminating to carry out similar investigations in other systems for which HPS data are available, such as alkali atoms in various buffer gases. A knowledge of the relationship of theoretical to experimental results in these systems would disclose the generality of the behavior observed for N-He and thus clarify the relative importance of correlation and other effects in interacting atomic systems.

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Calculation of the Electron Binding Energies and X-Ray Energies for the Superheavy Elements 114, 126, and 140 Using Relativistic Self-Consistent-Field Atomic Wave Functions[*]

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Relativistic Hartree–Fock–Slater atomic wave functions have been calculated for the superheavy elements $Z = 114$ and 126. The calculations have been made both for the atom and for singly ionized states with holes in the K or L shells. A Wigner–Seitz boundary condition is used, and results for both point and finite nuclei are presented. From these solutions, binding energies and x-ray energies have been evaluated. Similar calculations have been made on Au and U, and have been compared with experiment so as to ascertain what degree of confidence one may have in these computations. A discussion is made of the importance of finite nuclear size in determining the K-shell binding energy, and a solution for element 140 was obtained to demonstrate the atomic stability in the present approximation of elements above $Z = 137$. Finally, the probability for finding an electron within the nuclear radius is given for each of the elements studied, and a brief discussion is given concerning the stability of the superheavy elements against electron capture.

I. INTRODUCTION

There has recently been much speculation[1] about the formation of the superheavy elements ($Z = 114$, $A = 298$) and ($Z = 126$, $A = 310$), which because of their doubly magic numbers may exist with relatively long half lives. If such isotopes could be made, there is the likelihood that in the decay of the excited nuclear states, inner-shell vacancies of the atom, particularly the K shell, would be formed that would subsequently lead to the emission of characteristic x rays. The energy of an internally converted electron will also depend on the binding energies. These x-ray and binding energies might be used to identify the elements if they exist, perhaps in remnants of supernovae or as a product of heavy ion bombardment. In addition, a comparison of the experimental x-ray energies with calculations based on a finite nucleus might yield an estimate of the nuclear size.

We have calculated relativistic self-consistent-field (SCF) wave functions for the elements $Z = 114$ and 126. For these calculations, we have solved the Dirac equation numerically for a self-consistent field with spherical symmetry and Wigner-Seitz boundary conditions. A Slater-type electron exchange approximation, and both point and distributed nuclear charges were used. From the eigenvalues of the solutions for neutral atoms, one can estimate the energies of the x rays which would be emitted following an inner-shell vacancy. In addition, $K\alpha_{1,2}$ x-ray energies have been calculated from the difference in the total energies of the appropriate one-hole configurations. Calculations on gold and uranium have also been made, and have been compared with the experimental results to determine the accuracy of our program for x-ray energy calculations. Finally, an evaluation is made of the dependence of the atomic binding energies on the nuclear size and diffusivity.

In a discussion of superheavy elements, those with $Z > 137$ have always been of special interest. The Darwin-Gordon[2,3] solution of the Dirac equation for a point nuclear charge breaks down for $Z > 1/\alpha$, where α is the fine-structure constant. An earlier investigation[4] by Werner and Wheeler has shown that, with a nuclear charge distribution of finite size, a K-shell electron may exist with a stable electronic configuration where $Z > 1/\alpha$. There remained, however, a degree of uncertainty on account of the approximate nature of that investigation, which did not include, among other things,