

Effects of the Coulomb Correlation on the Calculated Results for Atoms with and without Spin Polarization*†

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In this paper we present the results of some atomic calculations as affected by the Coulomb correlation. We deal with atoms and ions with and without spin polarization. Thus we are able to compare calculated energy eigenvalues and hyperfine fields of contact with the experimental ionization energies and fields. Our approximation for the mass operator (exchange plus correlation) can thus be compared with the approximations proposed by Slater, Gaspar, Kohn and Sham, and Liberman. A broad evaluation of the results implies that our approximation for exchange and correlation is correct. Furthermore, when neglecting the correlation effects, we noticed that the results become poorer. Thus, this paper favors a single-particle description of many-body systems based on an effective-wave equation with the mass operator instead of the simpler exchange operator of the Hartree-Fock theory.

I. INTRODUCTION

In the present paper we report some results of atomic calculations on light elements, using some different approximations for exchange energy. Our purpose is to compare the many exchanges among themselves and with the experimental data available for these elements. We are specially interested in studying an approximation (X_M) for the mass operator proposed by one of the authors,¹ and in comparing the results from this approximation with those derived from the exchange energies proposed by Slater (X_S),² Gaspar,³ and Kohn and Sham (X_C),⁴ and Liberman (X_L).⁵ All these approximations for the exchange energy or the mass operator⁶ have the common feature of being based on the eigenvalues of these operators for the free-electron gas. The mass operator differs from the exchange operator in that in the former the effects of Coulomb correlation are included. In Liberman's approach (X_L) as well as in Ferreira's approach (X_M), the exchange energy is made dependent on the local electronic speed. In Slater's (X_S) and Gaspar-Kohn-Sham's (X_C) approaches, this speed dependence is eliminated by averaging over the occupied states of the free-electron gas (X_S) or by taking the exchange eigenvalue at the Fermi surface (X_C). We decided to exclude from our study the so-called X_α exchange,⁷ because this approach is based on the adjustment of a parameter to fit the calculated results to the experimental values. As it will be seen in the last section of the present work, one merit of the X_M operator is to suggest that in a X_α approximation, α should be chosen in the range 0.67–1.00,

as it has been actually found in many calculations.^{8,9} We also exclude from our study the recent proposal by Herman *et al.*¹⁰ of an exchange depending on the local gradient of the charge density. This new exchange operator has the merit of going beyond the strict scope of the free-electron gas approximation, but for this very reason is not comparable to X_M , X_L , X_S , and X_C . Thus we could say that the whole idea behind the present investigation is to study how well the free-electron gas approximation can be used in inhomogeneous systems, if one also includes into the exchange operator the effects due to the Coulomb correlation.

In Sec. II we reintroduce the X_M approximation,¹ and extend it to spin-polarized systems. In Sec. III we discuss the modifications we had to make on a program due to Herman and Skillman,¹¹ in order to be able to use X_M and spin polarization. In Sec. IV we discuss the results (energy eigenvalues) for atoms with no spin polarization. Because the energy eigenvalues are not truly comparable to the experimental ionization energies, we decided to make calculations for the hyperfine field of contact in spin-polarized ions. This field is related to the spin density at the nucleus and can be measured with relative ease. Thus in Sec. V we present the calculated results for this field and compare them with the measured fields.

II. MASS OPERATOR IN SPIN-POLARIZED SYSTEMS

A local approximation to the mass operator can be obtained from the real part of the eigenvalue of this operator in the free-electron gas. For an excitation with wave vector \vec{k} in a gas with Fermi

momentum k_F , one obtains

$$e(\vec{K}) = -\frac{1}{\pi^2} \int \frac{d^3k}{k^2} \theta(E_F - E_{\vec{k} + \vec{K}}) \operatorname{Re} \left[\frac{1}{\epsilon(\vec{k}, E_{\vec{k} + \vec{K}} - K_0)} \right] + \frac{1}{\pi^3} \int_{k_0 \geq 0} \frac{d^4k}{k^2} \operatorname{Im} \left(\frac{1}{\epsilon(\vec{k}, k_0)} \right) P \frac{1}{E_{\vec{k} + \vec{K}} - K_0 + k_0}, \quad (2.1)$$

where $K_0 = K^2$, $E_{\vec{k}} = k^2$, and $E_F = k_F^2$. The first term can be readily interpreted as the exchange energy due to the Coulomb interaction screened by the dielectric constant ϵ . If one uses $\epsilon = 1$ one obtains from the first term in the right-hand side of Eq. (2.1) the exchange energy in a free-electron gas. The main effect of a dielectric constant is to screen the Coulomb interaction thus reducing the exchange energy. In Fig. 1 we compare the first term in the right-hand side of Eq. (2.1) for a random-phase approximation (RPA) dielectric constant¹² and for

$$\operatorname{Re} \left[\frac{1}{\epsilon(\vec{k}, E_{\vec{k} + \vec{K}} - K_0)} \right] = \frac{1}{1 + k_{FT}^2/k^2}, \quad (2.2)$$

where k_{FT} is the Fermi-Thomas wave number

$$k_{FT} = (4k_F/\pi)^{1/2}, \quad (2.3a)$$

with

$$k_F = (3\pi^2 n)^{1/3}. \quad (2.3b)$$

This latter assignment for ϵ leads to an integrated expression as in Eq. (8. a) of Ref. 1 and here reproduced as

$$e(\vec{K}) \Big|_{1st \text{ term}} = -\left(\frac{2}{\pi}\right) \left[k_F + \frac{k_F^2 + k_{FT}^2 - K^2}{4K} \ln \frac{(K + k_F)^2 + k_{FT}^2}{(K - k_F)^2 + k_{FT}^2} + k_{FT} \left(t g^{-1} \frac{K - k_F}{k_{FT}} - t g^{-1} \frac{K + k_F}{k_{FT}} \right) \right]. \quad (2.4)$$

The comparison shown in Fig. 1 shows that the expression given by Eq. (2.4) is valid for computational purposes. The second term in the right-hand side of Eq. (2.1) represents a shift in the excitation frequency due to the absorption in the electron gas. This term has a negligible dependence on the wave vector \vec{K} of the excitation. In Fig. 2 we plot the behavior of this term as a function of the Fermi wave number k_F , in the range corresponding to the electronic densities one encounters in atomic and band calculations. One sees from the figure that the following empirical approximation is valid:

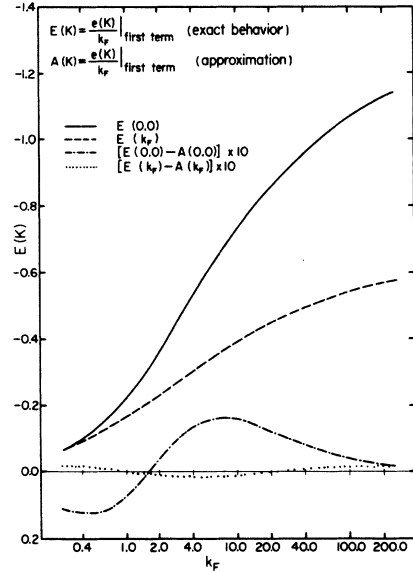


FIG. 1. Exact behavior of the first term of Eq. (2.1), $E(K)$, as a function of k_F when compared with the approximation given by Eq. (2.4), $A(K)$.

$$e(K) \Big|_{2nd \text{ term}} = 0.054 k_F \theta(129 - k_F) \ln(k_F/129). \quad (2.5)$$

When using Eqs. (2.4) and (2.5) in band or atomic calculations, one considers both k_F and K as functions of position through the local electronic density $n(\vec{r})$ [Eq. (2.3b)], and through

$$K^2 = (\text{energy eigenvalue}) - v(\vec{r}) - e(\vec{K}). \quad (2.6)$$

Thus one obtains a local approximation for the mass operator in the form of a potential energy.

In order to account for the spin polarization in atoms and crystals, one must generalize the theory above. We consider a molecular field H acting on the electron gas. Depending on the spin direction, the electronic energies and excitation frequencies become

$$E_{\vec{k}} = k^2 \pm \gamma H, \quad (2.7)$$

$$K_0 = K^2 \pm \gamma H, \quad (2.8)$$

while the dielectric constant is

$$\epsilon = 1 + \frac{1}{2} [(\epsilon_+ - 1) + (\epsilon_- - 1)], \quad (2.9)$$

where ϵ_{\pm} is the dielectric constant of a gas of up (down) spins. Thus the molecular field H entails a modification in the dielectric constant which is second order in H , and therefore small. In trying to observe the effect of spin polarization upon the dielectric constant and through it the effect upon the calculated energy levels of the spin-polarized atomic shells, we considered that Eqs. (2.9) and (2.2) lead to an effective Fermi-Thomas wave number

$$k_{FT}^2(\text{effective}) = \frac{1}{2} k_{FT}^2(+) + \frac{1}{2} k_{FT}^2(-), \quad (2.10)$$

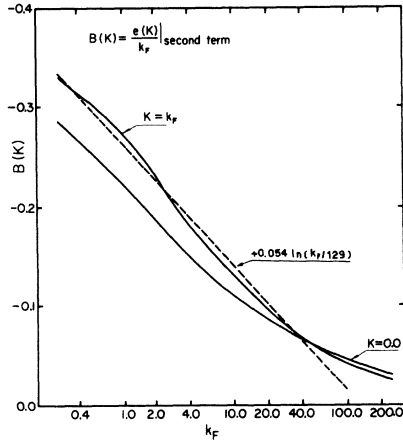


FIG. 2. Exact behavior of the second term of Eq. (2.1) $B(K)$, as a function of k_F (solid lines) when compared with the approximation given by Eq. (2.5) (dashed lines).

where $k_{FT}(\pm)$ are to be calculated from Eq. (2.3) for the different electronic densities of the up- and down-spin gases. *From these calculations we concluded that spin polarization had no effect upon the electronic energies through a change in the dielectric constant.*

Thus considering that ϵ and $E_{\vec{k}} + \vec{k} - K_0$ are not affected by spin polarization, the second term in the right-hand side of Eq. (2.1) does not change due to any reasonable degree of spin alignment. For this term, the approximation given by Eq. (2.5) remains valid if k_F is calculated from the total (up- and down-spin) electronic density.

In the first term in the right-hand side of Eq. (2.1), the spin alignment does appear in the argument of the θ function through

$$E_F - E_{\vec{k}} + \vec{k} = k_F^2 + \gamma H - |\vec{k} + \vec{K}|^2. \quad (2.11)$$

One sees that the introduction of a molecular field is analogous to using different Fermi wave numbers $k_{F(+)}$ and $k_{F(-)}$ for the two electronic gases. These Fermi wave numbers are to be calculated from

$$k_F(\pm) = (6\pi^2 n_{\pm})^{1/3}, \quad (2.12)$$

where n_{\pm} are the electronic densities for up (down) spins. Thus for each electronic gas with a different spin direction, the first term of the mass operator [Eq. (2.1)] should be calculated from Eq. (2.4) with $k_{F(\pm)}$ instead of k_F , but with k_{FT} calculated from the total electronic density through Eqs. (2.3a) and (2.3b).

III. COMPUTATIONAL TECHNIQUES

The following results were obtained by means of a program described by Herman and Skillman.¹¹ This program, which calculates self-consistently atomic orbitals and energy levels, was adapted to

our machine and to the problem of an exchange interaction (mass operator) dependent on the eigenvalues through Eq. (2.6). The main modifications were as follows:

(a) The criterion of self-consistency was imposed upon the Coulomb potential instead of upon the total potential (Coulomb plus exchange).

(b) After a certain loop of self-consistency, the exchange potential to be used in the next loop was calculated based on the eigenvalues determined in the preceding loop.

(c) In the case of spin polarization, since we needed good wave functions at the nucleus (see Sec. V), we had to increase the precision of the calculation by requiring a higher degree of self-consistency. In one case we had to use the FORTRAN double precision feature.

The mass operator described in Sec. II is not defined if $K(\gamma)^2 \leq 0$. In Ref. 1, one of the authors suggested the use of an analytical continuation to the expression given by Eq. (2.4). This continuation was tested by us and shown to generate important errors due to its singular behavior at $K^2 = -\infty$. Therefore, we followed Liberman⁵ and took the value of $e(K)$ at $K=0$ whenever $K^2 \leq 0$. Unlike Liberman, for $K^2 \geq k_F^2$ we take the value of $e(K)$ according to Eqs. (2.4) and (2.5), instead of $e(k_F)$.

The finding of K^2 through Eq. (2.6) presents a problem in that K^2 is dependent on $e(K)$ itself. To solve this problem we used two procedures.

(i) At a given loop of self-consistency, we use in the right-hand side of Eq. (2.6) the exchange of the preceding loop to calculate K^2 . This procedure gives "exact" results but leads to a slower convergence than in the "inexact" procedure described below.

(ii) Instead of $e(K)$ in the right-hand side of Eq. (2.6) we use Slater's approximation²

$$e(K)_{\text{Slater}} = -3k_F/\pi. \quad (3.1)$$

For the reader's convenience, we compare in Table I some results obtained by using the exact technique, X_M , with those obtained by using the inexact technique, X_{MS} . It will be noted that they are very similar.

IV. RESULTS FOR ATOMS WITHOUT SPIN POLARIZATION

Table II exemplifies some typical numerical results obtained by us. The column labeled by X_{HF} represents the results of an exact Hartree-Fock calculation. X_L gives the results for Liberman's approach to exchange.⁵ This latter exchange is equal to ours if we neglect the second term in the right-hand side of Eq. (2.1) and make $k_{FT} = 0$ in Eq. (2.4). X_S represents Slater's approximation given by Eq. (3.1). X_M is the present approximation to the screened exchange interaction (mass operator). X_G is the Gaspar-Kohn-Sham exchange,^{3,4} which is

TABLE I. Eigenvalues for Mg (rydbergs).

	X_M	X_{MS}
1s	93.55	93.54
2s	5.801	5.764
2p	3.294	3.294
3s	0.404	0.402

exactly $\frac{2}{3}$ of the value given by Eq. (3.1).

Table II was constructed in such a way that columns with larger entries are placed to the left. One notices that, as a rule, the entries corresponding to the mass operator (X_M) seem to be between those of X_S and X_G . The X_M eigenvalues corresponding to the deep levels are closer to the X_S values, while for the shallow levels they are closer to the X_G entries. The X_L values are very close to the exact HF values. This fact shows that Liberman's way to localize the exchange operator, and consequently our way to localize the mass operator, is a very good one.

The experimental values are not truly comparable to the calculated values. As it is well known, the eigenvalue of a single-electron wave equation can only be interpreted as an ionization energy when the number of electrons is very large (Koopman's theorem).¹³ For a finite number of electrons, the ionization energy, which is the experimental result, should be larger than the eigenvalue. When the number of electrons is not large, the wave equation is at best a means for determining the electronic wave functions. Since the eigenvalues obtained in X_{HF} , X_L , and X_S are larger than

TABLE III. Overlap integrals.

Ion	Shell	X_L	X_M
A	1s-2s	0.00123 ^{a,b}	0.00082
	1s-3s	0.00002 ^{a,b}	0.00014
	2s-3s	0.00029 ^{a,b}	0.00184
Cu [*]	2p-3p	0.00386 ^{a,b}	0.00006
	1s-2s	0.0014 ^c	0.0004
	1s-3s	0.0003 ^c	0.0000
	2s-3s	0.0040 ^c	0.0010
	2p-3p	0.0017 ^c	0.0004

^aCalculated by us.

^bFrom Ref. 5.

^cFrom J. C. Slater, Timothy M. Wilson, and J. H. Wood, Phys. Rev. **179**, 28 (1969). Actually the overlap for Cu^{*} was calculated from an approximation for exchange slightly different from X_L .

the experimental ionization energies, one could expect that the corresponding wave functions are defective to some extent. In the Appendix we describe a procedure to obtain energies which should be comparable to the experimental ionization energies.

Another point worth mentioning is related to the fact that when using X_L and X_M one obtains non-orthogonal orbitals. Table III presents some overlap integrals for the ions A and Cu^{*}. In the case of X_L , this overlap is a defect coming from the localization of the exchange operator. Indeed, the true HF exchange does not depend on the eigenvalue but it is only through its localization that this dependence appears. In the case of X_M , by analogy with X_L , one could say that part of this

TABLE II. Energy eigenvalues calculated according to different approximations for the exchange interaction (rydbergs).

Ion	Shell	X_{HF}	X_L	X_S	Expt ^a	X_M	X_G
Mg ^b	1s	...	97.63	94.95	96.38	93.55	91.90
	2s	...	7.452	6.552	6.60	5.801	5.80
	2p	...	4.535	4.144	3.80	3.294	3.43
	3s	...	0.401	0.505	...	0.404	0.431
A ^c	1s	238.26	237.22	233.46	236	230.94	228.42
	2s	24.82	24.64	22.96	23.6	22.12	21.62
	2p	19.14	19.18	18.14	18.1	17.15	16.76
	3s	2.574	2.344	2.072	1.87	1.705	1.682
	3p	1.180	1.060	1.006	0.915	0.694	0.666
Cu ^d	1s	658.22	656.17	650.41	...	658.54	642.27
	2s	82.26	81.81	78.88	...	80.794	77.01
	2p	71.86	71.79	69.74	...	71.314	67.69
	3s	10.65	10.37	9.357	...	9.542	8.84
	3p	7.284	7.078	6.431	...	6.457	5.942
	3d	1.620	1.410	1.461	...	1.210	1.131

^aSee J. A. Bearden and A. F. Burr, Rev. Mod. Phys. **39**, 125 (1967).

^bFor this ion, all numerical results were obtained by us.

^cFor this ion, except for the column X_M , all the results were taken from Ref. 5.

^dFor this ion, except for the column X_M , all the results were taken from J. C. Slater, Timothy M. Wilson, and J. H. Wood, Phys. Rev. **179**, 28 (1969).

TABLE IV. Contact field (χ) for different ions and exchange energies.

Ion	X_{HF}	X_L	X_S	Expt	X_M	X_G
N	0.73 ^a	3.22	1.40	0.40 ^b	0.40	1.5
Na	8.05 ^a	9.36 ^c	7.55	...
P	-0.59 ^d	1.81	0.56	0.38 ^d	0.72	...
V ⁺⁺	-3.8	-2.3 ^e	-2.8	-1.9
				-3.0 ^e		
Mn ⁺⁺	-3.34 ^d	2.8	-4.24	-3.1 ^f	-3.6	-2.3
				-2.1 ^g		
				-2.9 ^e		
Fe ⁺⁺	-3.29 ^d	...	-4.39	-3.1 ^f	-4.0	...
				-2.1 ^g		
Ni ⁺⁺	-3.94 ^d	8.0	...	-3.0 ^e	-4.1	-2.9

^aFrom D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

^bFrom L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. **116**, 87 (1959).

^cFrom P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

^dFrom Ref. 16.

^eResults for 0 coordination. See P. R. Locher and S. Geschwind, Phys. Rev. Letters **11**, 333 (1963); S. Geschwind, Bull. Am. Phys. Soc. **8**, 212 (1963). In the case of Fe, these results refer to Fe⁺⁺⁺ and not to Fe⁺⁺. The entry on the table is, in this case, an extrapolated value for a different ionicity.

^fSame as (e) but for F coordination.

^gSame as (e) but for S coordination.

overlap comes from the localization of the mass operator. On the other hand, unlike the exchange operator, the true mass operator is eigenvalue dependent,⁶ and a non-null overlap should be expected even in the case of the exact solution of the effective wave equation for the quasiparticle.

V. RESULTS FOR SPIN-POLARIZED IONS

When dealing with spin polarization one must generalize the approximations for the exchange energy in order to differentiate up spins from down spins. This generalization, in the case of the mass operator (X_M), has been described in Sec. II. In the case of X_L and X_G , it is sufficient to use $k_F(\pm)$ defined by Eq. (2.12) instead of k_F defined by Eq. (2.3b). We shall now obtain different orbitals in a same atomic shell for different spin directions. A convenient parameter, readily comparable to the experimental result, is the effective magnetic field H_c for the contact interaction between the electronic shells and the nucleus. This field H_c is paramount in determining the hyperfine structure of the ion. According to Abragam and Pryce,¹⁴ this field H_c can be written as

$$H_c (\text{gauss}) = 4.21 \times 10^4 \chi (\text{a. u.}), \quad (5.1)$$

where

$$\chi = (4\pi/2S) \sum_n [|\phi_{ns+}(0)|^2 - |\phi_{ns-}(0)|^2], \quad (5.2)$$

and where S is the total electronic spin, and $\phi_{ns\pm}(0)$ are the s -electron wave functions at the nucleus for the different spin orientations.

In Table IV we present the numerical results for χ and different ions. It will be noted that in no

case are the calculated results in complete agreement with the experimental values. There are two important reasons to believe that the entries in the column "experiment" are not very reliable themselves.

(i) These entries are obtained from measurements taken from ions dissolved in crystalline matrices. The crystalline potential affects the ion to some extent, as one can see from the entries for Mn⁺⁺ and Fe⁺⁺ and for different coordinations. Thus, the measured values are not truly comparable to the calculated values, which refer to free ions.

(ii) In the spin-polarization theory, the ionic ground state is not an eigenstate of the total spin operator. This inconsistency of the theory may be expected to generate errors which do affect the value of χ .¹⁵

In Fig. 3 we reproduce the results for χ obtained by Freeman and Watson¹⁶ for the transition series, and add some results obtained by us. From this figure and from Table IV it will be seen that again the results calculated with X_M stand between those from X_G and X_S .

VI. CONCLUSIONS AND DISCUSSION

Although the real test for an approximation for the exchange energy should come from band calculations, the atomic calculations are still of value because they can be easily made and self-consistency attained. In the present attempt, we tried to compare the four approximations X_L , X_G , X_S , and X_M based on the simple idea of using the free-electron gas results for each small element of volume. An approximation for exchange such as that

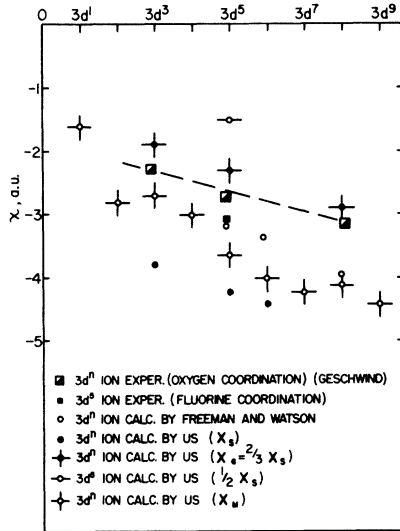


FIG. 3. Hyperfine field of contact (χ) for the transition series.

proposed by Herman *et al.*¹⁰ is beyond the scope of the present investigation in that it also considers the effect of local gradients of the charge density.

In a broad evaluation of our tables, we could say that the results are such that

$$\text{Res}(X_L) \cong \text{Res}(X_S) \cong \text{Res}(X_M) \cong \text{Res}(X_G), \quad (6.1)$$

where Res means results for. The experimental results, when comparable to the calculated values, seem to be such that

$$\text{Res}(X_S) \cong \text{Res}(\text{expt}) \cong \text{Res}(X_G), \quad (6.2)$$

where Res means results for; in other words, in the same range of the results calculated with X_M . Other authors have also reached the same conclusion.⁸ Indeed, it is becoming increasingly popular to use the so-called X_α exchange, where

$$(X_\alpha) = \alpha(X_S) = -3\alpha k_F/\pi. \quad (6.3)$$

Although α varies with the problem in question, it has been found that it usually lies between $\frac{2}{3}$ (exchange X_G) and 1 (exchange X_S). It thus seems that one merit of X_M is to confirm, in terms of the mass operator, the otherwise empirical X_α method.

Another important conclusion can be derived from a comparison of the X_L and X_M results. X_L and X_M differ only in the fact that in X_M the correlation energy is also included while X_L is strictly a Hartree-Fock approximation. The X_M results are near the experimental values, while the X_L results are not. Thus one sees that a single-particle description of a many-body system can be improved by going beyond the Hartree-Fock theory and into the realm of the effective wave equation for the quasiparticles.

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APPENDIX: AN APPROXIMATE WAY TO CALCULATE IONIZATION ENERGIES IN ATOMS

In Sec. IV we explained why the calculated one-electron eigenvalues could not be expected to match the experimental ionization energies. Only in the limit of an infinite number of electrons the Koopman's theorem becomes valid and the eigenvalues and the ionization energies coincide. In any many-body theory, the eigenvalue E_i of the one-electron effective-wave equation is interpreted as a change in the total energy of the system due to a removal or addition of a particle in the quasiparticle state Ψ_i . Equivalently, we could write that the eigenvalue E_i is defined by

$$E_i = \frac{\partial \langle E \rangle}{\partial n_i}, \quad (A1)$$

where $\langle E \rangle$ is the total energy of the system, and n_i is the occupation number of the state Ψ_i .

For systems with a finite number of electrons, such as atoms and ions, we assume that Eq. (A1) is still valid by allowing for the possibility of a fractional occupation number n_i .¹⁷ Then, the eigenvalue E_i becomes a function of the occupation number n_i , and the ionization energy becomes

$$\text{ionization energy} = \langle E \rangle_{n_i} - \langle E \rangle_{n_i-1} = \int_{n_i-1}^{n_i} dx E_i(x). \quad (A2)$$

Thus the ionization energy can be obtained if the energy eigenvalues $E_i(x)$ are known for several occupations x in the interval $(n_i, n_i - 1)$.

The program for atomic calculations devised by Herman and Skillman may be readily adapted to

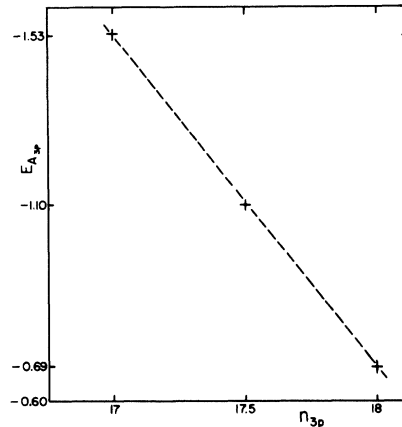


FIG. 4. Behavior of the energy eigenvalue of the argon 3p shell as a function of the occupation number n_{3p} .

TABLE V. Ionization energy of the $3p$ electrons of A.
In rydbergs.

$\int X_M$	Expt	X_M
1.1	0.92	0.69

situations with fractional occupation numbers. Figure 4 and Table V summarize well our results. It will be noticed that the eigenvalue $E_t(x)$ is a quasilinear function of the occupation x . Thus the

integral in Eq. (A2) is simply the value of the integrand at half-occupation

$$\text{ionization energy} \cong E_t(n_t - 0.5). \quad (\text{A3})$$

Table V compares the ionization energy obtained in this method ($\int X_M$) with the experimental value and the eigenvalue at full occupation (X_M). One sees that, though the calculated energy is now shifted in the correct direction with respect to the eigenvalue, the shift is too large thus leading to a calculated energy larger than the experimental value.

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Positron Annihilation and Positronium Bubbles in Liquid and Solid Argon, Krypton, and Xenon*

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The angular correlations of photons from positrons annihilating in liquid and solid argon, krypton, and xenon show positronium-bubble formation in the liquid phase but not in the solid. Positronium formation increases with increasing atomic weight while bubble radii decrease with increasing atomic weight.

INTRODUCTION

Considerable interest has recently been shown in the theoretical problems¹⁻⁵ posed by the observation^{6,7} that positronium (Ps) atoms and electrons are confined to a localized or "bubble" state in the liquified inert gases. The experiments have shown, as Ferrell first postulated,⁸ that a Ps atom in a liquid of inert molecules blows itself a bubble of such size that the zero-point pressure of the Ps

atom and the hydrostatic forces (surface tension and pressure) are balanced. The diameter of such a bubble in liquid helium is quite large, about 40 Å. Liquids with larger surface tension develop smaller bubbles, viz., about 15 Å in liquid argon. The relative ease of understanding these experiments at a simple level and the similarity of the Ps and electron problem gives one increased confidence in the basic features of the bubble picture, and points to several more detailed experimental