lisions of metastable He with Ar has been report-
ed in the literature.[6,7] Moreover, in recent ex-
periments[8] we noticed a strong temperature de-
pendence of the intensity ratio $HeAr^+/Ar^+$, a fact
which also would be expected from the electron
energy distribution observed.

Much new information about the details of Re-
actions (1) and (3), namely about the ionization
probability as a function of the separation be-
tween A^* and B and about the interaction forces
before and after the ionization, is contained in
electron energy distributions as shown in Figs.
1 and 2. Since no valid theory is available to ex-
tract this information, we attempt to explain the
measured distributions in terms of potential en-
ergy curves of the collision system before and

after the ionization, the ionization itself being
considered fast compared with the relative mo-
tion of the heavy particles. More experimental
data and a detailed discussion will be published.

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BRUECKNER-GOLDSTONE MANY-BODY THEORY
FOR THE HYPERFINE STRUCTURE OF PHOSPHORUS*

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The Brueckner–Goldstone many-body perturbation theory is utilized to study the hy-
perfine interaction in atomic phosphorus. By this method, a correlation contribution to
the hfs constant of a positive sign and an appropriate magnitude is obtained, which pre-
dominates over the negative core-polarization effect to produce substantial agreement
with experiment.

The hyperfine structure constant in atomic
phosphorus ($3p^3$; ^4S) has been recently measured
carefully by both atomic-beam[1] and optical-pump-
ing[2] techniques to be $A = +55.055\,691 \pm 0.000\,007$
Mc/sec. In contrast, unrestricted Hartree-Fock
(UHF) and related approaches[3] all lead to a nega-
tive sign with values ranging from -42 Mc/sec to
-132 Mc/sec. This sharp disagreement between
theory and experiment has led to some doubts
concerning the validity of the UHF procedure
and, indeed, the core-polarization concept in
general.[3] It is the purpose of the present note to
present the results of a Brueckner-Goldstone-
type[4] (BG) calculation of the hfs in atomic phos-
phorus, which shows that a proper treatment of
correlation effects provides the requisite posi-
tive contribution which in combination with the
negative core-polarization effect leads to a good
agreement between theory and experiment with
respect to both magnitude and sign.

The BG procedure has earlier been successful-
ly applied to the hfs calculations of He (^3S),[5] Li
(^2S ground state[6] and ^2P excited state[7]), and the
nitrogen atom[8] (^4S). The advantages of the BG

procedure for the study of hfs effects are mani-
fold. First, being a perturbation theory, it han-
dles small numbers rather than differences of
large numbers as one does in conventional UHF
calculations, where the difference of large up-
and down-spin densities are evaluated.[3,8] Fur-
ther, the technique allows a convenient separa-
tion of physical effects such as core polarization,
consistency, and various types of correlation,
and permits a systematic handling of such effects
through diagrammatic field-theoretical tech-
nique. These advantages, plus its success with
the light atoms, particularly nitrogen,[9] where
one had a similar uncertainty in the theoretical
situation in the magnitude of A, though not in
sign, prompted us to apply this procedure to the
phosphorus atom.

Since the BG procedure, both in its application
to the hfs[5-8,10,11] problem as well as to other
properties[12] of atoms, has been discussed elabo-
rately in the past, we shall only mention a few
brief facts to facilitate the description of our re-
sults.

The total Hamiltonian $\mathcal{K}$ for the atom can be

separated into an unperturbed part, $\mathcal{H}_0$, and a perturbation, $\mathcal{H}'$, given by

$$\mathcal{H}_0 = \sum_{i=1}^{N} T_i + \sum_{i=1}^{N} V_i, \tag{1}$$

$$\mathcal{H}' = \sum_{i>j} r_{ij}^{-1} - \sum_i V_i, \tag{2}$$

where T_i is the sum of the kinetic-energy and nuclear-Coulomb-potential operators, and V_i represents the single-particle potential for the ith electron. In our calculation, we utilized the Hartree-Fock type V^{N-1} potential.[12] The complete orthonormal set $\{\varphi_i\}$ of one-electron bound and continuum states is generated by solving the equation

$$(T + V)\varphi_i = \epsilon_i \varphi_i. \tag{3}$$

The s states were generated in the Hartree-Fock field of a neutral phosphorus atom with a 3s electron removed. Thus, the one-electron 3s state from Eq. (3) is identical with the Hartree-Fock 3s state, while the 1s and 2s states differed slightly from the true Hartree-Fock states. The

non-s states (p, d, and f) were generated in the field of the neutral atom minus a 3p electron. The unperturbed many-electron ground state Φ_0 is given by a Slater determinant formed with the lowest N solutions φ_i. The true ground-state wave function Ψ_0 is then given by

$$\Psi_0 = \sum_{n=0}^{\infty} L[(E_0 - \mathcal{H}_0)^{-1}\mathcal{H}']^n \Phi_0$$

$$\equiv |0\rangle + |1\rangle + \cdots + |n\rangle + \cdots |m\rangle + \cdots, \tag{4}$$

where

$$E_0 = \sum_{i=1}^{N} \epsilon_i$$

and L denotes that only "linked" terms[4] are to be added. The contact hfs operator for an atom is

$$O_{\text{hfs}} = \frac{16\pi}{3}\beta\mu_N \sum_{i=1}^{N} \delta(\vec{r}_i)\vec{s}_i \cdot \vec{I}, \tag{5}$$

where the symbols have their usual meaning. The hfs constant A for an S-state atom is then given by

$$A = \frac{16\pi}{3}\frac{\beta\mu_N}{IS}\frac{\langle\Psi_0|\sum_{i=1}^{N}\delta(\vec{r}_i)s_{zi}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} = \frac{16\pi}{3}\frac{\beta\mu_N}{IS}\frac{\{\langle 0|f|0\rangle + \langle 0|f|1\rangle + \cdots + \langle m|f|n\rangle\}}{\{\langle 0|0\rangle + \langle 1|1\rangle + \cdots + \langle m|n\rangle + \cdots\}}, \tag{6}$$

where

$$f = \sum_{i=1}^{N} \delta(\vec{r}_i)s_{zi}, \tag{7}$$

and I and S are the total nuclear and electronic spins. Each term in Eq. (6) can be represented by a group of Feynman-like diagrams drawn according to the rules described earlier[6,8,10,12] with suitable notation for hole and particle states and interaction vertices. In taking the expectation value only the linked-cluster expansion for the atomic wave function Ψ_0 is used; Eq. (6) will yield some unlinked diagrams, as illustrated in Fig. 1(j). Also, Eq. (6) gives diagrams of the type Fig. 1(k), where a hfs vertex connects two different hole lines; that is, $j \neq j'$ only. In Fig. 1, the vertex connecting wavy lines represents O_{hfs}. The downward and upward lines represent hole and particle states, respectively, while the vertex connecting dashed lines represents the interaction r_{12}^{-1}.

The most important diagrams contributing to

hfs are presented in Figs. 1(a)-1(i), and their values are listed in Table I. These values include the effect of the normalization factor in the denominator of Eq. (6), which came out to be 1.0040 including up to second order. The (0, 1) diagrams in Fig. 1(c) describe core-polarization effects. The corresponding values in Table I include the effects of hole-hole and hole-particle ladder corrections[6,8,10] which occur for 1s and 2s diagrams. The individual contributions from 1s, 2s, and 3s states are seen to be similar in nature and sign as in the UHF calculations, although there are differences in magnitude. Our total core-polarization result is -64.596 Mc/sec, and again the negative sign is in agreement with the UHF calculation.[3]

The important (1, 1) diagrams in Figs. 1(b) and 1(c) represent correlation effects describable as mutual polarization of 3p and 3s orbitals and 3p and 2p orbitals. Fig. 1(c) is just the exchange counterpart of Fig. 1(b). The correlation between 3p and 3s was found to be much larger than
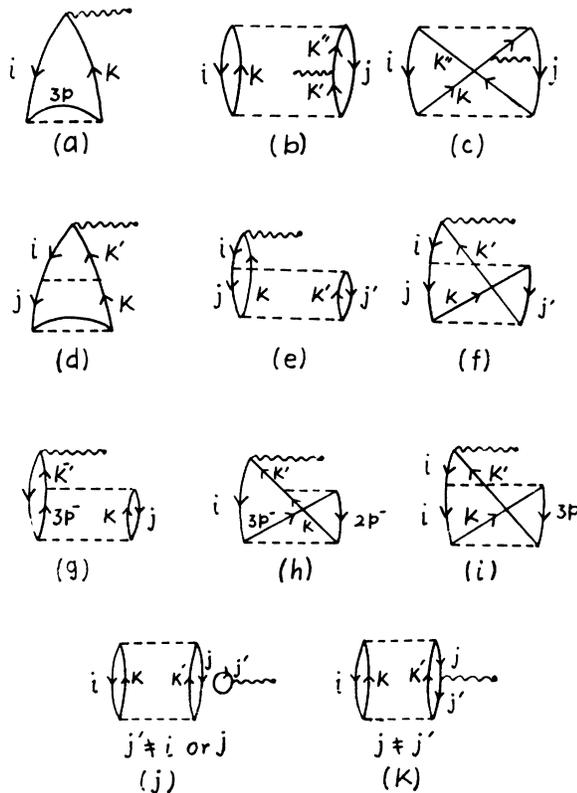
FIG. 1. Hfs diagrams for phosphorus. Only those diagrams which make major contributions to the hfs constant are presented.

that between $3p$ and $2s$ or $1s$. This is a result of the stronger overlap between $3s$ and $3p$ orbitals. Correspondingly, $3p$ and $2p$ correlate significantly because of the angular character. The total contribution from the diagrams 1(b) and 1(c) is 19.662 Mc/sec. In addition, there are twenty-some other diagrams which produced a total contribution of -4.987 Mc/sec. Among these, in particular, are contributions from the unlinked diagrams, Fig. 1(j), and the nondiagonal hole-hole diagrams, Fig. 1(k), plus their respective exchange counterparts. Considerable numerical cancellation occurs among these diagrams and their sum is only -0.618 Mc/sec in our case. Moreover, the individual values of these 1(j) and 1(k) diagrams are quite small and do not exceed 2.4 Mc/sec. The net result from the (1, 1) diagrams is 14.674 Mc/sec.

Of the (0, 2) diagrams, Fig. 1(d) really represents higher order effects associated with core polarization. Thus, the first two rows of Table I for this class of diagrams represent the indirect core polarization of the $2s$ electron by the $3p$ electron mediated by $3s$ and $2p$ states, respec-

tively. The other two rows represent consistency effect combined with core polarization. For example, the third row describes the effect of the exchange interaction between the $3p$ electrons, while one of them is core polarizing the $1s$ state. The next class of (0, 2) diagrams are those indicated in Figs. 1(e) and 1(f). The former represents effects of correlation between $3p$ and $3s$ states of a different nature than in 1(b). Figure 1(f) is the exchange counterpart of 1(e). Figure 1(g) represents the influence of the correlation between $3s^+$ and $3s^-$, which will vanish by spin cancellation except for the fact that $3p^-$ state is not occupied while $3p^+$ state is. Thus, 1(g) is a residue diagram, as is also 1(h), which represents the correlation effect between $2p^-$ and $3s^-$ and $2p^-$ and $2s^-$ states. The greater contribution from $2p^-$ and $2s^-$ states relative to the $3s^-$ state can be understood by the substantial overlap between states of the same principal quantum number. The last important (0, 2) diagram is 1(i) which, in the language of earlier literature,[6,8,12] is an exclusion-principle-violating diagram. It results from our choice of V^{N-1} potential. In both (0, 2) as well as (1, 1) diagrams, hole-hole ladder corrections are applied to $1s$, $2s$, and $2p$ hole lines wherever necessary. Hole-particle ladder corrections, which are more difficult to calculate and usually smaller,[8,12] have been neglected. In addition to the (0, 2) diagrams shown in Fig. 1, there are ninety-nine other diagrams which contribute 4.364 Mc/sec as compared with 95.352 Mc/sec from diagrams 1(d)-1(i).

Thus the (1, 1) and (0, 2) diagrams lead to the combined positive contribution of 114.390 Mc/sec, which overwhelms the negative core-polarization contribution. However, it is more appropriate to combine diagram 1(d) with diagram 1(a) since the former represents higher order effects of consistency combined with core polarization. The total core-polarization contribution then adds adds up to -52.384 Mc/sec, while correlation effect contribution is 102.179 Mc/sec. With either of these processes of combining the diagrams, we get for the theoretical hfs constant $A = 49.795$ Mc/sec. The remaining difference of 5.261 Mc/sec could arise from several sources. Thus, we have neglected hole-particle and particle-particle ladder corrections in both (1, 1) and (0, 2) diagrams as well as higher diagrams. Experience with these effects in lighter atoms,[6-8,10] particularly nitrogen, indicates that these sources could provide a substantial part of the remaining 5.261

Table I. Contributions from various hfs diagrams.

Order	Diagram	Description	Contribution (Mc/sec)
(0,1)	1(a)	i = 1s	-111.342
		i = 2s	145.620
		i = 3s	-98.874
	Total		-64.596
(1,1)	1(b)	i = 3s, j = 3p	3.017
		i = 2p, j = 3p	4.321
	1(c)	i = 3s, j = 3p	9.885
		i = 2p, j = 3p	2.438
Other (1,1)			-4.987
	Total		14.674
(0,2)	1(d)	i = 2s, j = 3s	-4.118
		i = 2s, j = 2p	13.693
		i = 1s, j = 3p	-35.959
		i = 2s, j = 3p	38.595
	1(e)	i = 3s, j = 3p, j' = 3s	23.310
	1(f)	i = 3s, j = 3p, j' = 3s	35.025
	1(g)	i = 3s, j = 3s	-14.636
	1(h)	i = 2s	29.106
		i = 3s	-18.792
	1(i)	i = 1s	-2.712
		i = 3s	31.839
Other (0,2)			4.365
	Total		99.716
	Grand total		+49.795
	Experiment		+55.055 691$\pm$0.000 008

Mc/sec. Secondly, there could be significant contributions of the right order from relativistic effects. It should be remarked that the type of relativistic effects involved here is different from that usually associated with the direct contribution from valence electrons,[13] which is zero in the present case. Instead, we are concerned with the influence of relativistic effects on the contribution of the core s electrons through their core polarizations and correlations with the valence electrons. A proper treatment of such effects would require a BG many-body formalism in terms of Dirac theory.

In conclusion, it has been demonstrated that core-polarization effects in phosphorus have definite physical origin and meaning. Secondly, they are dominated by correlation effects of opposite sign, which restore agreement with experiment. Finally, the BG formalism permits a convenient and reliable procedure for calculation of both these effects. It would be desirable to test if the conclusions obtained here concerning the importance of correlation effects can also be arrived at by other many-body procedures such as the Bethe-Goldstone method, which has been applied successfully[14] in the past to other atoms.

Further, it would be interesting to apply the BG procedure to study other atoms such as arsenic and antimony, which have similar np^3 valence configurations as nitrogen and phosphorus, as well as transition-metal atoms[15] like manganese and iron, where the net core-polarization contribution is small because of strong cancellations between various core s states.

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EXACT COMPUTATION OF THE VAN DER WAALS CONSTANT FOR TWO HYDROGEN ATOMS*

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An exact formula is obtained for C_{HH}, the van der Waals constant which appears in $V_{HH} = -C_{HH}/R^6$, the London potential for two hydrogen atoms. Numerical evaluation gives $C_{HH} = 6.499\,026\,7 \pm 0.000\,000\,4$.

The London potential acting between two neutral atoms A and B, $V_{AB}(R) = -C_{AB}/R^6$, is of central importance in the theory of atomic interactions at low energies. As a consequence, approximate computations of the van der Waals constant C_{AB} have been carried out for a variety of atoms over a period of many years.[1] The purpose of this note is to show that for the case of two hydrogen atoms, the prototype of all atom-atom interaction problems, an exact computation of C_{HH} is possible. We present below an analytic formula for C_{HH}, from which a highly accurate numerical value is readily obtained.

C_{HH} may be written as the sum of a bound-state contribution $C_{HH}^{(b)}$ and a continuum contribution $C_{HH}^{(c)}$:

$$C_{HH} = C_{HH}^{(b)} + C_{HH}^{(c)}, \qquad (1a)$$

where

$$C_{HH}^{(b)} = -\tfrac{2}{3}e^4 \sum_{n=2}^{\infty} P(2W_1 - W_n)R_n \qquad (1b)$$

and

$$C_{HH}^{(c)} = \frac{2}{3}e^4 \int_{-W_1}^{\infty} \frac{dw}{\pi} P(-w + W_1) \operatorname{Im} P(w + W_1). \qquad (1c)$$

Here $W_n = -\alpha^2 m/2n^2$ ($n = 1, 2, \cdots$) are the bound-state energies, $P(E)$ is defined, for complex E, by

$$P(E) = \langle \varphi_0 | \vec{\mathbf{x}} \cdot (E - H)^{-1} \vec{\mathbf{x}} | \varphi_0 \rangle, \qquad (2)$$