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Extended Use of the Coulomb Approximation: Mean Powers of r, a Sum Rule, and Improved Transition Integrals

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Expectation values of r and of r^2 have been computed for a range of effective quantum numbers up to 8.5 by use of Coulomb-approximation wave functions. The results show that the hydrogenic formulas for these expectation values are accurate for noninteger quantum numbers ν to better than 1% for all $\nu-l>1.0$, and much greater accuracy is attained for larger ν. The sum rule wherein the squares of the dipole radial transition integrals sum to $\langle r^2\rangle$ can therefore be used with the hydrogenic formula for the latter quantity as an excellent approximation for all but small ν. A number of radial dipole integrals for calculating transition probabilities are obtained for O I, O II, O III, and O IV by use of the Hartree-Hartree-Swirles wave functions for the lower state and Coulomb-approximation functions for the excited states. The results are compared with analytic Hartree-Fock and Hartree-Fock-Slater values, and with the results of Stewart and Rotenberg. Some effects of configuration interaction are noted in the case of O II. Particular attention is paid to the contribution to the dipole integrals from large distances which present calculations omit or evaluate inaccurately. To demonstrate this problem, a few dipole integrals for O I, O II, and N I are computed more accurately.

1. INTRODUCTION

In a now very well-known paper, Bates and Damgaard[1] tabulated, in effect, values of the radial transition matrix element, or dipole integral,

$$\sigma=\frac{1}{(4l_>^2-1)^{1/2}}\int_0^\infty R_iR_fr^3dr\,, \tag{1}$$

where $l_>$ is the greater of the angular momenta belonging to the initial and final states with radial wave functions R_i and R_f, respectively. The asymptotic form of bound-state Coulomb wave functions was employed on the basis of the idea that, for large numbers or classes of transitions of many atoms, the contribution to the dipole integral from the region of space near the origin, where this form is invalid, is small. They showed that, for many states, the one-electron potential reaches its asymptotic Coulombic form before the region is reached which gives the dominant contribution to the dipole integral. This approximation is particularly good for nonequivalent electrons, and for excited states where the tendency for the contribution to the dipole integral to arise from large distances is enhanced.

The conjecture by Bates and Damgaard, wherein they established a normalization for their Coulomb wave functions, has been at least partially resolved by Foldy[2] and by Seaton.[3] Foldy employed effective-range theory (later extended by Norman[4] and by Moiseiwitsch[5]) to derive the normalization correction for $l=0$ states, and Seaton, using analyticity properties of the wave function as a function of the energy, gave the same result without the restriction on angular momentum.

The considerations of Seaton and Foldy are still limited to the assumption of separability and the existence of a single-particle potential which is independent of energy. If a one-electron potential is assumed but allowed to depend on energy, then it can be shown[6] that the normalization correction $\zeta(\nu)\equiv1+\partial\mu/\partial\nu$ given by Seaton and Foldy is modified to become

$$\zeta_1(\nu)\equiv\zeta(\nu)\bigg/\left(1+\tfrac{1}{2}\nu^3\int R_{nl}^2\frac{\partial v(\epsilon,r)}{\partial\nu}r^2dr\right), \tag{2}$$

where $v(\epsilon,r)$ is the one-electron potential and ν is the effective quantum number $(C^2/\epsilon)^{1/2}$, where ϵ is the one-electron energy parameter and C is the residual charge on the ionic core. The quantum defect μ is given by $n-\nu$ where n is the appropriate integer. This type of correction could be particularly important for equivalent-electron states, which would involve considerable rearrangement of the remaining equivalent electrons if one of them is promoted to an inequivalent state. This rearrangement, in turn, would lead effectively to an energy-dependent potential. In any event, the correc-

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[1] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. London **A242**, 101 (1949).

[2] L. L. Foldy, Phys. Rev. **111**, 1093 (1958).

[3] M. J. Seaton, Monthly Notices Roy. Astron. Soc. **118**, 504 (1958).

[4] G. E. Norman, Opt. i Spektroskopiya **12**, 333 (1962) [English transl.: Opt. Spectry. (USSR) **12**, 183 (1962)].

[5] B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **79**, 1166 (1962).

[6] B. H. Armstrong, unpublished. See P. S. Kelly, J. Sokoloff, and B. H. Armstrong, Air Force Weapons Laboratory (Kirtland Air Force Base, New Mexico) report No. TR 64–172, Part III (1965) (unpublished).

tion to the hydrogenic normalization constant used by Bates and Damgaard is small for high states, with which we shall be primarily concerned in this paper.

2. MEAN POWERS OF r

In addition to being useful in determining transition integrals, the Coulomb approximation (CA) can, of course, be used to determine mean powers of the radius r defined as

$$\langle r^n\rangle_i \equiv \int_0^\infty r^n R_i^2 r^2 dr. \qquad (3)$$

In a footnote to their paper (p. 111 of Ref. 1), Bates and Damgaard state that it is sufficient to employ the effective quantum number ν in the hydrogenic formula for $\langle r^2\rangle$:

$$\langle r^2\rangle_{\mathrm{CA}} \cong (\nu^2/2C^2)[5\nu^2+1-3l(l+1)], \qquad (4)$$

where the subscript CA has been appended to denote that this formula is expected to approximately reproduce the CA value. Although it was not explicitly stated in their paper, one can surmise that this statement was made in realization of the high degree of insensitivity of $\langle r^2\rangle$ to the details of the wave function. This is to be expected since there is no cancellation in this integral as there is in the transition integral, Eq. (1), and since $\langle r^2\rangle$ is less dependent yet than $\langle r\rangle$ or the transition integral on the contribution from the region of space near the origin. This behavior is amply borne out in atomic diamagnetic-susceptibility calculations, where one finds that even screening-constant determinations of $R(r)$ yield rather good results.[7] The explicit motivation for the Bates-Damgaard footnote was the fact that $\langle r^2\rangle$ can be used in approximate electron-collision cross section determinations as might be needed, e.g., for line-broadening estimates in astrophysical studies. This quantity is still of interest in approximate line-broadening calculations based on the more modern Baranger[8] results for the impact broadening width, since the sum rule for the transition integrals given by Bethe and Salpeter,[9]

$$\sum_{n'} (R_{nl}{}^{n',l-1})^2 = \sum_{n'} (R_{nl}{}^{n',l+1})^2 = \langle r^2\rangle_{nl}, \qquad (5)$$

can be used to approximately evaluate the Baranger formulas [Eqs. (113) and (128) of Ref. 8]. This approximate evaluation is useful for high states in line-merging studies,[10] but to our knowledge, the quantitative accuracy of the hydrogenic expression for $\langle r^2\rangle$ [i.e., Eq. (4)] has not been established for nonhydrogenic atoms. Although $\langle r^2\rangle$ is probably the most useful of the mean powers of r, other powers are occasionally of some importance. For example, $\langle r\rangle$ is sometimes used in the critical evaluation of variationally determined wave functions.[11] It is also of interest in approximate Stark-effect calculations as in the line-merging theory of Inglis and Teller.[12] If applied to other than hydrogen, the Inglis-Teller relation implies the use of $\langle r\rangle \cong n^2 a_0$ for nonintegral values of the quantum number n. It is therefore of interest to determine the accuracy of this approximation. In addition, $\langle r\rangle$ may be of value in other contexts such as approximate evaluation of expectation values of power-series expansions of functions of r.

Besides $\langle r^2\rangle$ and $\langle r\rangle$, we have also calculated values of the quasinormalization integral $\langle r^0\rangle$ since this latter quantity shows the "over-all" normalization of the CA wave function as used by Bates and Damgaard (viz., without the Seaton-Foldy correction) and since it may be of value in further studies of the normalization of CA wave functions. The definitions and method of computation of these quantities follow.

3. COULOMB-APPROXIMATION CALCULATION OF $\langle r^n\rangle$

The radial wave function in the Coulomb approximation is given by[1]

$$R(r) = K(\nu,l) r W_{\nu,l+1/2}(2Cr/\nu), \qquad (6)$$

where $\nu = C/\sqrt{\epsilon}$ is the effective quantum number, C is the residual ionic charge, l is the orbital angular momentum, and ϵ is the one-electron energy parameter, taken to be the ionization potential for inequivalent electrons. The normalization factor $K(\nu,l)$ is taken as in the original work of Bates and Damgaard to be for all ν the hydrogenic formula, which is

$$K(\nu,l) = \frac{C^{1/2}}{\{\nu^2\Gamma(\nu+l+1)\Gamma(\nu-l)\}^{1/2}}. \qquad (7)$$

For noninteger ν, a correction is necessary as previously discussed; however, such a correction is not included here. For the computation of $W_{\nu,l+1/2}(\rho)$, we have used the asymptotic representation

$$W_{\nu,l+1/2}(\rho) = \left(\frac{2\rho}{\nu}\right)^{\nu} e^{-\rho/\nu}\left\{1+\sum_{t=1}^{t_0}\frac{b_t(\nu,l)}{\rho^t}+O(\rho^{-t_0-1})\right\}, \qquad (8)$$

where

$$b_t = (\nu/2t)[l(l+1)-(\nu-t)(\nu-t+1)]b_{t-1}, \qquad (9)$$

and $b_0 = 1$. We have used this asymptotic form of W for all values of ρ since even the correct behavior of W has

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[7] Compare, e.g., E. C. Baughan, Trans. Faraday Soc. **59**, 2451 (1963).

[8] M. Baranger, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).

[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957).

[10] B. H. Armstrong, J. Quant. Spectry. Radiative Transfer **4**, 207 (1964).

[11] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

[12] D. R. Inglis and E. Teller, Astrophys. J. **90**, 439 (1939).

no significance for small ρ.[13] The formula

$$R(r)=K(\nu,l)r\left(\frac{2Cr}{\nu}\right)^{\nu}e^{-Cr/\nu}\left[1+\sum_{t=1}^{t_0}\frac{b_t(\nu,l)}{(Cr/\nu)^t}\right] \tag{10}$$

then defines our CA wave function. We truncate the series in Eq. (10) at the minimum term (for each value of ρ). This will cause a small difference between our results and results obtained by strict use of the Bates-Damgaard formulas. The use of this asymptotic expansion for W rather than the true Whittaker function may also have a significant effect on the normalization, particularly where the CA has only marginal validity, i.e., where the non-Coulombic part of the potential has a long tail. In the original work of Bates and Damgaard, Eq. (10) was used to compute analytically a doubly infinite series for the dipole integral σ. This double series for σ was then truncated at a judiciously chosen term (independent of r), rather than the series for the wave function itself, as we have done here.

Our calculations were programmed in FORTRAN II and carried out on an IBM 7090 digital computer. The computations were organized to maintain an accuracy of somewhat better than 1 part in 10^5 in the asymptotic representation of the Whittaker function (and the gamma functions involved). For small effective quantum number our results for the Whittaker function can be readily compared with the results tabulated by Curtis.[14] For radii r of two and four Bohr radii, effective quantum number $\nu=1.58114$, residual charge $C=2$ ($x\equiv Cr=4$ and 8), $l=1$, the results compare as follows for the Whittaker function $W_{\nu,3/2}(2Cr/\nu)$:

r	Program, asymptotic series	Curtis, exact function
2.0	1.30852	1.30851
4.0	0.275944	0.275943

The integrations yielding the mean second power of r, and the mean first power for large ν, were adjusted to maintain an accuracy of just better than 1 part in 10^5 (in view of the accuracy of the Whittaker function). Thus, the total error from this and the squared Whittaker function should not exceed 2 to 3 parts in 10^5, and the tabular entries, which have been rounded to four figures, should be accurate to all figures with perhaps an occasional error of one unit in the last place. In the case of $\langle r^1\rangle$ for small ν, and for the quantity $\langle r^0\rangle$, this accuracy was difficult to maintain without excessive computation. Since it is unlikely that CA results for the small ν values of these quantities are of sufficient physical significance to warrant this effort, the accuracy was lowered here.

TABLE I. Representative values of the Coulomb-approximation pseudonormalization integral $\langle r^0\rangle$, defined by Eq. (11) of the text, for various values of orbital angular momentum l and effective quantum number ν.

	$\langle r^0\rangle$		
$\nu-l$ \ $l=$	0	1	2
1.2	0.995	0.969	0.982
1.4	0.989	0.975	1.024
1.6	0.989	0.997	1.057
1.8	0.995	1.010	1.045
2.2	0.999	0.989	0.984
...	...	...	...
6.5	0.9962	0.9964	0.995

The reason for the problem is as follows: Near $r=0$, the series on the right-hand side of Eq. (10), which modulates the otherwise smoothly varying exponential behavior of the W function, does not contribute, viz., it is unity. At some relatively small value of r, it discontinuously begins to contribute (on account of our truncation procedure) with a rather large value, and then rapidly settles down to a slowly varying behavior. It is this discontinuous effect at small r that makes an accurate calculation of $\langle r^0\rangle$ and $\langle r^1\rangle$ for small ν difficult and not too meaningful.

The asymptotic formula for $R(r)$, given by Eqs. (9) and (10) reduces to the expression for the hydrogen eigenfunctions when the quantum number ν is an integer. Hence, all values of $\langle r^n\rangle_{\mathrm{CA}}/\langle r^n\rangle_{\mathrm{hyd}}$ are unity for integral ν. Since this affords a convenient check on most of the calculational procedures, a number of such $\langle r^n\rangle$ values were computed. The errors in the ratios to hydrogenic values were typically one to two digits in the seventh figure.

The effects of truncating the asymptotic series for the Whittaker function as previously described should be borne in mind. For small ρ, the value for $W_{\nu,l+1/2}$ obtained by this procedure will be quite different from that of the true Whittaker function. The singularity at $\rho=0$ present in the true Whittaker function (for noninteger ν) is effectively removed by this truncation procedure, so that the truncated function is similar to a real physical wave function, behaving properly at the origin even though its values for small r are not meaningful. The results of Table I indicate that it is even rather well normalized in the "over-all" sense, viz., when the spurious inner region is included. The inaccurate behavior of the truncated wave function a short distance away from the origin shows up somewhat in the quasinormalization integral

$$\langle r^0\rangle=K^2(\nu,l)\int_0^\infty W_{\nu,l+1/2}{}^2(2Cr/\nu)r^2dr$$

since there is no power of r to decrease the integrand at small r and increase it at large r in the fashion required for the validity of what is usually meant by the "Cou-

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[13] For the standard CA to be meaningful, the results must ultimately become independent, or nearly independent, of the behavior of the wave function for small values of the radial variable. Therefore, the precise prescription for the wave function at small ρ is arbitrary.

[14] A. R. Curtis, *Coulomb Wave Functions* (Royal Society Mathematical Tables) (Cambridge University Press, Cambridge, England, 1964), Vol. 2.

TABLE II. Representative values of the mean first power of r in the Coulomb approximation for various values of orbital angular momentum l and effective quantum number ν.

		$\langle r^1 \rangle$	
$\nu - l$ \ $l=$	0	1	2
0.8	1.0027	1.0061	1.049
1.2	1.0003	0.9959	0.991
1.4	1.0004	0.9958	0.997
1.6	1.0001	0.9980	1.004
1.8	1.0000	1.0000	1.0045
...	...	...	...
6.5	0.9999	0.9999	0.9998

lomb approximation." The values of the mean first power of r when applied to a specific atomic state should have a similar validity to the usual CA for dipole transition integrals although improved somewhat due to lack of cancellation. The mean second power in the CA as implied previously should have much greater accuracy, both on account of the lack of cancellation and on account of the additional power of r. Explicitly, the quantities calculated are

$$\frac{\langle r^n \rangle_{\text{CA}}}{\langle r^n \rangle_{\text{hyd}}} \equiv \frac{K^2(\nu,l) \int_0^\infty r^n [W_{\nu,\, l+1/2}]^2 r^2 dr}{\langle r^n \rangle_{\text{hyd}}}, \tag{11}$$

where $\langle r^n \rangle_{\text{hyd}}$ is given by

$$\begin{aligned} \langle r^0 \rangle_{\text{hyd}} &= 1, \\ \langle r^1 \rangle_{\text{hyd}} &= \tfrac{1}{2}[3\nu^2 - l(l+1)], \\ \langle r^2 \rangle_{\text{hyd}} &= \tfrac{1}{2}\nu^2[5\nu^2 + l - 3l(l+1)]. \end{aligned} \tag{12}$$

Explicit tabulations of these quantities have been carried out up to ν equal to 8.5. The results are contained in an unpublished report[15] (which may be obtained upon request from the author), and we merely summarize them here, since the value of the numbers presented lies not so much in their usefulness *per se*, but in the fact that they provide direct numerical evidence of the accuracy of the hydrogenic formulas. Table I gives a few values for $\langle r^0 \rangle$ for $l=0$, 1, 2 which are sufficient to indicate the order-of-magnitude of the departures from unity. Between the omitted $\nu - l$ values of 2.2 and 6.5, and beyond 6.5, the results converge toward unity with slow oscillations. Table II contains representative values of $\langle r^1 \rangle$; as might be expected, these are much closer to unity. This quantity also shows slow oscillations as ν increases, but with much reduced amplitude. Finally, Table III shows the behavior of $\langle r^2 \rangle$; this quantity is, of course, much closer yet to unity. For $l=0$ and 1, all values beyond those shown (viz., $\nu - l > 1.8$) are unity to four figures. For $l=2$, $\langle r^2 \rangle$ becomes equal to unity (to 4 figures) at $\nu - l = 2.8$ and remains so thereafter.

The close agreement between the "hydrogenic values" of $\langle r \rangle$ and $\langle r^2 \rangle$ as given by Eq. (12), and the CA values, which our results demonstrate, indicates that for most practical purposes it will be quite adequate to utilize (for these and any higher powers of r) the hydrogenic formulas with noninteger values of ν for excited states of atoms other than hydrogen. (In spite of the accuracy of the hydrogenic formulas towards surprisingly low values of ν, the results will not be useful unless the normalization correction $\zeta = 1 + \partial\mu/\partial\nu$ is unimportant. This may not be the case for low-lying states.) Our calculations then provide a measure of the error involved over a range of ν values that should cover most cases of practical interest. It is evident that the sum rule given in Eq. (5), valid for any atom having a single transition electron,[9] can now be extended to

$$\sum_{n'} (R_{nl'}{}^{n'l-1})^2 = \sum_{n'} (R_{nl'}{}^{n'l+1})^2$$

$$\cong \tfrac{1}{2}\nu^2 a_0[5\nu^2 + 1 - 3l(l+1)] \tag{13}$$

with a high degree of accuracy for states n for which the CA is valid.

4. DIPOLE TRANSITION INTEGRALS FOR OXYGEN IONS

As noted above, the CA has proved to be an effective and reliable method for the calculation of dipole radial integrals [as defined by Eq. (1)] for certain classes of transitions.[1,16] However, for transitions involving equivalent electrons in low-lying or ground terms there is an ambiguity in the choice of energy parameter and also a substantial correction to the normalization becomes necessary.[3] Although one can argue that the proper energy parameter should be the ionization potential to the appropriate parent term,[6] such an argument is not of much practical value. The reason is that it turns out that such transitions substantially involve the spatial region where the potential is non-Coulombic and therefore the conditions necessary for the validity of the CA are not met. At least this is the case for the $2p^q$ states of oxygen and nitrogen and it may be true in general. Also, the normalization correction for the ground or

TABLE III. Representative values of the mean second power of r in the Coulomb-approximation for various values of orbital angular momentum l and effective quantum number ν.

		$\langle r^2 \rangle$	
$\nu - l$ \ $l=$	0	1	2
0.8	0.9931	0.9994	1.0064
1.2	0.9999	0.9999	0.9981
1.4	0.9999	0.9998	0.9987
1.6	1.0000	0.9998	0.9998
1.8	1.0000	1.0000	1.0003

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[15] These may be obtained from the author, B. H. Armstrong, IBM Scientific Center (Palo Alto, California) Technical Report, (1966) (unpublished).

[16] See, e.g., M. D. Kunisz, Acta Phys. Polon. 22, 99 (1962).

TABLE IV. $R_{\text{H-F}}(r)/R_{\text{CA}}(r)$, the ratio of H-F and CA wave functions for $l=1$. The species and state are designated at the head of each column as is the effective quantum number ν determined from the H-F orbital energy. The CA wave functions have been computed from Eq. (10) and in addition the normalization correction factor $\zeta(\nu)=(\nu-1)(\nu+2)/\nu(\nu+1)$ has been used.

$\nu=$ r	OI[a] $2p^4(^3P)$ 0.8898	OI[b] $2p^4(^3P)$ 0.8897	OI[a] $2p^4(^1S)$ 0.9490	OII[a] $2p^3(^4S)$ 1.228	OII[b] $2p^3(^4S)$ 1.228	OII[b] $2p^3(^2P)$ 1.296	OII[a] $2p^3(^2P)$ 1.296	NI[c] $2p^3(^4S)$ 0.9424	NI[b] $2p^3(^4S)$ 0.9387	NI[c] $2p^3(^2P)$ 1.031	OIII[b] $2p^2(^3P)$ 1.483
0.2	1.18	1.100	1.32	1.054	0.9847	1.186	1.185	0.971	0.9670	1.17	0.4569
0.4	0.299	0.2988	0.293	0.3731	0.3731	0.3782	0.3783	0.236	0.2372	0.236	0.4733
0.6	0.551	0.5501	0.520	0.6043	0.6044	0.5968	0.5970	0.453	0.4555	0.427	0.6630
0.8	0.742	0.7418	0.692	0.7627	0.7631	0.7322	0.7319	0.641	0.6451	0.593	0.7809
1.0	0.880	0.8811	0.812	0.8709	0.8712	0.8161	0.8158	0.793	0.7980	0.719	0.8536
1.2	0.984	0.9856	0.895	0.9469	0.9465	0.8698	0.8702	0.914	0.9203	0.812	0.9006
1.4	1.06	1.066	0.949	1.000	0.9994	0.8976	0.9051	1.01	0.9768	0.879	0.930
1.6	1.12	1.115	0.989	1.039	1.038	0.9277	0.9287	1.08	1.088	0.926	0.9564
1.8	1.16	1.155	1.02	1.068	1.068	0.9450	0.9452	1.14	1.144	0.960	0.9742
2.0	1.19	1.187	1.04	1.090	1.091	0.9582	0.9572	1.19	1.190	0.987	0.9879
2.2	1.21	1.213	1.05	1.107	1.110	0.9685	0.9659	1.22	1.227	1.01	0.9986
2.4	1.23	1.234	1.06	1.121	1.124	0.9764	0.9728	1.25	1.258	1.02	1.007
2.6	1.25	1.252	1.07	1.132	1.135	0.9821	0.9785	1.27	1.285	1.03	1.012
2.8	1.26	1.266	1.08	1.141	1.143	0.9855	0.9825	1.29	1.307	1.04	1.015
3.0	1.27	1.277	1.09	1.148	1.147	0.9867	0.9860	1.31	1.326	1.05	1.017
3.2	1.28	1.284	1.09	1.15	1.148	0.9856	0.9888	1.32	1.341	1.05	1.016
3.4	1.29	1.288	1.09	1.16	1.146	0.9823	0.991	1.34	1.353	1.06	1.013
3.6	1.29	1.288	1.10	1.16	1.142	0.9769	0.992	1.35	1.362	1.06	1.009
3.8	1.3	1.285	1.1	1.17	1.135	0.9696	0.995	1.36	1.367	1.07	1.002
4.0	1.3	1.278	1.1	1.17	1.125	0.9605	0.997	1.36	1.370	1.07	0.9954
4.5	1.3	1.246	1.1	1.18	1.092	0.9303	0.996	1.4	1.362	1.1	0.9705
5.0	1.3	1.199	1.1	1.2	1.048	0.8924	0.999	1.4	1.338	1.1	0.9400
5.5	1.3	1.138	1.1	1.2	0.9982	0.8487	1.0	1.4	1.299	1.1	0.9087
6.0	1.3	1.069	1.1	1.2	0.9422	0.8009	1.0	1.4	1.249	1.0	0.8623
6.5	1	0.9949	1	1.3	0.8791	0.7510	1.0	1.4	1.191	1.0	0.8132
7.0	1	0.9183	1	1.3	0.8354	0.6978	1	1.5	1.127	1.0	0.8042

[a] H-F function from Ref. 24.
[b] H-F function from Ref. 22 (the number of figures given does not imply a corresponding accuracy).
[c] H-F function from Ref. 25.

low-lying terms is difficult to obtain accurately from experimental data due to the large extrapolation in energy that is required. There are, of course, other ways of calculating dipole integrals between these low-lying terms and higher states. More and more Hartree-Fock (H-F) and analytic or approximate H-F results are becoming available for excited states,[17–19] and other semiempirical methods have been developed[20] which can account more accurately for the core region than can the customary CA. However, these methods tend to follow the general rule that more accuracy requires more labor, and the increase in labor can be quite severe. In order to account for such transitions without an undue increase in labor over the usual CA, it is proposed herein to use the CA only for the excited state in the dipole integral, and to use a H-F function or other more accurate function for the ground state (or low-lying term). Hartree-Fock or analytic Hartree-Fock (AHF) ground state wave functions are now available for all light atoms and a number of heavy ones.[21–23] Thus, the only calculations involved in our proposal are those of the CA wave functions and of the numerical integration. Both of these are straightforward, particularly with the availability of a digital computer. The results obtained in this way still depend on a contribution from the core region more substantially than do the "proper" CA dipole integrals. However, the error arising from this contribution is significantly reduced by use of the more correct ground-state function. Also, as one proceeds towards final states of higher excitation, the core contribution should diminish as the upper wave functions become more diffuse. Thus, our approximation improves for such states. Those transitions for which the CA was already marginal, e.g., may then be accounted for rather accurately. Table IV (taken from Ref. 6) lends some support to this view; it shows ratios of H-F to CA wave functions for some of the $2p^q$ low-lying ground terms of O and N. In interpreting this table it should be

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[17] P. S. Kelly, Astrophys. J. **140**, 1247 (1964).

[18] P. S. Kelly, J. Quant. Spectry. Radiative Transfer **4**, 117 (1964).

[19] C. Froese, Phys. Rev. **137**, A1644 (1965).

[20] J. C. Stewart and M. Rotenberg, Phys. Rev. **140**, A1508 (1965).

[21] A list of such calculations up to 1947 has been given by Hartree: Rept. Progr. Phys. **11**, 113 (1948). See also D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[22] C. C. J. Roothaan and P. S. Kelly, Phys. Rev. **131**, 1177 (1963).

[23] E. Clementi, IBM J. Res. Develop. **9**, 2 (1965).

TABLE V. Comparison of H-F and H-F Coulomb-approximation dipole-integral contributions by spatial regions: p-s and p-d transitions of OI, OII, and NI. The CA function for the lower ($2p$) state has been asymptotically normalized to the corresponding HF function in each case. The lower state for the OI transition is $2p^4(^3P)$, and for the NI and OII transitions it is $2p^3(^4S)$.

	OI Transition				NI Transition		OII Transition	
Upper state →	$2p^3(^4S)3d(^3D)$		$2p^3(^4S)3s(^3S)$		$2p^2(^3P)3d(^4P)$		$2p^2(^3P)3d(^4P)$	
Region	$\Delta\sigma$ (H-F)	$\Delta\sigma$ (HFCA)	$\Delta\sigma$ (H-F)	$\Delta\sigma$ (HFCA)	$\Delta\sigma$ (H-F)	$\Delta\sigma$ (HFCA)	$\Delta\sigma$ (H-F)	$\Delta\sigma$ (HFCA)
$r=0$–1.2	0.00074	0.00196	−0.03053	−0.1163	0.0010	0.0069	0.0085	0.0280
$r=1.2$–4.0	0.03056	0.03185	0.25192	0.2440	0.0432	0.0645	0.1035	0.1200
$r=4.0$–9.0	0.02209	0.02211	0.09991	0.1000	0.0377	0.0360	0.0130	0.0128
$r=0-\infty$	0.05339	0.05592	0.32130	0.2280	0.0819	0.1074	0.1250	0.1608

borne in mind that the asymptotic behavior of some of the analytic H-F functions is poorly determined (this appears to be especially true of $2p$ functions). Four figures have been given in these cases since the authors did not specify the number of figures to correspond to the accuracy of the functions, as was done in the numerical H-F calculations we have referenced. The H-F orbital energy parameter has been used to determine the effective quantum numbers for the Coulomb approximations to the H-F functions. The absolute values of the ratios given in Table IV are of no accurate significance; the relative variation is the quantity of significance. For these computations the approximate normalization correction $\zeta(\nu)=(\nu-1)(\nu+2)/\nu(\nu+1)$ suggested by Seaton[3] was employed to avoid the divergence of the hydrogenic normalization function [given in Eq. (7)] at $\nu=1$. It should be pointed out that the OII $2p$ function of Table IV, column 7, is the Hartree-Hartree-Swirles function without configuration interaction. This same ratio has also been computed for some $3s$ and $3d$ state analytic Hartree-Fock functions.[17] These ratios have been given elsewhere[6,15] and will not be repeated here except to note that the asymptotic ratios in these latter cases are considerably closer to unity than for the $2p$ functions shown in Table IV. In fact, for all the $3s$ states for which these ratios were computed, the ratios were within 6% of unity and for all the $3d$ states computed, the ratios were within 1% of unity. Table V gives the contributions to the radial dipole integral σ from three spatial regions, $r=0$–1.2, 1.2–4.0, and 4.0 to 9.0, for H-F wave functions and for CA wave functions. Again, the H-F orbital energy parameter has been used to determine the effective quantum numbers for the Coulomb approximations to the H-F functions. For these calculations of Table V the CA functions for the lower ($2p$) states have been normalized to agree asymptotically with the corresponding H-F functions. This result is accordingly labeled HFCA. The HF dipole integrals utilize Hartree[24,25] ground-state functions with Kelly's[17] AHF upper state functions. By such direct comparisons of Hartree-Fock and CA wave functions we see that the CA wave functions are systematically too large in absolute value in the inner "core" region (probably due to a component of the irregular solution present in the true Whittaker function which is not completely removed by our truncation procedure). Thus, we should be able to improve the value of σ by improving the $2p$-function, even if the upper function is not improved. Also, it is the $2p^q$ states that have the large (and uncertain) normalization correction. The higher states have a much smaller normalization correction which for approximate purposes can usually be disregarded (and we do here).

(a) Numerical Procedures

The upper-state wave functions were computed according to Eq. (10) by the method described previously. The integration of σ was carried out by Simpson's rule on the interval grid of the Hartree-Hartree-Swirles[24] (HHS) functions. The error due to this integration procedure was estimated to be substantially less than the error which arises from the uncertainty in the HHS functions. The accuracy of these latter functions drops off rapidly with increasing r, while the contribution to the dipole integral remains significant. On this account, an attempt was made to reduce this error by fitting the HHS functions asymptotically to CA wave functions. By this procedure, some of the roundoff error in the HHS functions can be smoothed out, and values obtained for radial distances beyond the HHS tabulation. This fitting was first attempted by using the effective quantum number determined by the Hartree-Fock orbital energy parameter (ϵ), given by HHS,[24] for the CA fit to the HHS functions. For OI ^3P, OII ^2P, and OIV ^2P this immediately yielded a constant asymptotic ratio of the two functions within the accuracy available (for the OI and OII ratios see columns 1 and 7 of Table IV). For the other functions, the ratios were not effectively constant at large r, and because of this, a strictly *ad hoc* adjustment was made in the effective quantum number until an adequate fit was achieved. Interestingly enough, for the OII ^2P HHS function with configuration interaction (and $\nu=1.284$) this procedure led back to 1.296, the same ν value as for the function *without* configuration interaction. This is demonstrated in Fig. 1 where the ratios of $R_{\text{H-F}}(r)/R_{\text{CA}}(r)$ are given as

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[24] D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. London **238**, 229 (1939).

[25] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).

a function of r for the ^2P function with configuration interaction for the original ν value of 1.284 (circles) and the adjusted ν value of 1.296 (squares). The ratios of the ^2P function without configuration interaction are repeated from Table IV for convenience, as triangles, and with higher accuracy (than is literally warranted). Unfortunately, the stated accuracy of the HHS functions at large r is not sufficient to enable one to draw definite conclusions from this phenomenon. It may be accidental since it requires believing the HHS functions to about one digit more than they gave. On the other hand, it is systematic over several values which lessens the probability that it is accidental. Perhaps the effect of the configuration superposition is to introduce a higher energy component into the wave function which dies out at large r. There appears to be no comparable explanation for the O II ^4S and O III ^3P states for which the adjusted ν values obtained were 1.245 and 1.500, respectively. In the O II ^4S state ratios for $r=7.0$ to 9.0 (not given in Table IV) there was much more scatter in values (from 0.95 to 2.5) than for the other states. In the case of the Ni ^4S state (columns 8 and 9 of Table IV) there appears an excessive departure from constancy in the asymptotic region. In this case there is probably a systematic error in the Hartree-Hartree function, as is also indicated by the large discrepancy between the Hartree effective quantum number and the analytic H-F effective quantum number—the latter should be accurate to 3 or 4 figures.

It should be pointed out that the numerical accuracy (the accuracy of the models employed is, of course, not known in general) of our results depends on the amount of cancellation present between the positive and negative contributions to the integrand. The separate positive and negative contributions can be easily monitored in the numerical procedures; however, since this has already been done by Kelly[17,18] for most of the states given here it was not felt worthwhile to repeat the effort. The difference between the positive/negative area ratios for Kelly's calculations and for those presented here should not be significant.

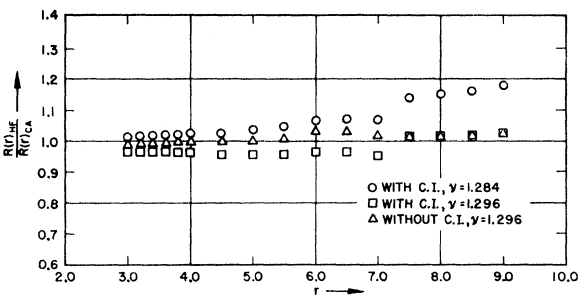

FIG. 1. Ratio of Hartree-Fock to Coulomb-approximation radial wave functions for the ^2P state of O II with configuration interaction (circles and squares) and without configuration interaction (triangles).

5. DIPOLE INTEGRAL RESULTS

Our results for O I and O IV are shown in Tables VI and VII and comparisons are indicated with the results of some other investigators. The most extensive available comparison data are those of Kelly.[18] For the $n=3$ states he has given analytic Hartree-Fock results which should be close to true H-F values. For most of the other states he has given the less accurate Hartree-Fock-Slater values; we list these for comparison. The results of Stewart and Rotenberg[20] can also be compared in the case of O IV. (For the lower stages of ionization, Stewart and Rotenberg have averaged over the different terms of the configuration involved.) The experimental effective quantum numbers for the upper states have

TABLE VI. Radial dipole integrals from the $2p^4(^3P)$ ground state of O I to the indicated upper states. The comparison values are: AHF–analytic Hartree-Fock[a]; HFS–Hartree-Fock-Slater.[18] The effective quantum numbers ν are from experimental term values except for the two, as indicated, which are from Hartree-Fock ϵ values.

Upper-state parameters ν	 Term	σ^2 (this calc.)	σ^2 (comparison)
1.849 (HF-ϵ)	$(^4S)3s(^3S)$	0.0785	0.0974 (AHF)
1.8224	$3s$	0.0965	0.152 (HFS)
2.8394	$4s$	0.0161	0.0171 (HFS)
3.8444	$5s$	6.9×10^{-3}	4.2×10^{-3} (HFS)
4.8466	$6s$	4.0×10^{-3}	1.6×10^{-3} (HFS)
5.8480	$7s$	1.6×10^{-3}	7.6×10^{-4} (HFS)
6.8487	$8s$	2.9×10^{-4}	4.3×10^{-4} (HFS)
7.8538	$9s$	5.2×10^{-6}	
8.8516	$10s$	2×10^{-6}	
2.999 (HF-ϵ)	$(^4S)3d(^3D)$	2.93×10^{-3}	2.59×10^{-3} (AHF)
2.9811	$3d$	5.01×10^{-3}	5.54×10^{-3} (HFS)
3.9798	$4d$	2.18×10^{-3}	3.71×10^{-3} (HFS)
4.9781	$5d$	9.6×10^{-4}	2.46×10^{-3} (HFS)
5.9778	$6d$	4.3×10^{-4}	1.52×10^{-3} (HFS)
6.9775	$7d$	1.7×10^{-4}	9.8×10^{-4} (HFS)
7.9873	$8d$	6.5×10^{-5}	6.7×10^{-4} (HFS)
8.9864	$9d$	1.5×10^{-5}	

[a] Reference 17. [b] Reference 18.

TABLE VII. Radial dipole integrals from the $2p(^2P)$ ground state of O IV to the indicated upper states. The comparison values are: AHF-Analytic Hartree Fock[a]; HFS-Hartree-Fock-Slater[b]; SR and BD-Stewart and Rotenberg, and Bates-Damgaard values.[c] The effective quantum numbers ν are obtained from Hartree-Fock ϵ values, from experimental term values, or are estimated.

Upper-state parameters ν	 Term	σ^2 (this calc.)	σ^2 (comparison)
2.5845 (HF-ϵ)	$(^1S)3s(^2S)$	0.0335	0.0372 (AHF)
2.5654 (expt)	$3s$	0.0386	0.0462 (HFS)
			0.031 (SR); 0.022 (BD)
3.5596 (expt)	$4s$	5.80×10^{-3}	5.59×10^{-3} (HFS)
4.5442 (expt)	$5s$	2.26×10^{-3}	1.64×10^{-3} (HFS)
5.520 (est)	$6s$	1.61×10^{-3}	6.8×10^{-4} (HFS)
2.947 (HF-ϵ)	$(^1S)3d(^2D)$	0.0401	0.0359 (AHF)
2.9276 (expt)	$3d$	0.0437	0.0396 (HFS)
			0.033 (SR); 0.032 (BD)
3.9274 (expt)	$4d$	9.09×10^{-3}	7.17×10^{-3} (HFS)
4.9258 (expt)	$5d$	3.44×10^{-3}	2.11×10^{-3} (HFS)
5.9245 (expt)	$6d$	1.52×10^{-3}	8.8×10^{-4} (HFS)
6.9235 (est)	$7d$	6.75×10^{-4}	4.7×10^{-4} (HFS)

[a] Reference 17. [b] Reference 18. [c] Reference 20.

TABLE VIII. Radial dipole integrals for various transitions of O and N. σ^2 (HF) indicates values obtained from the Hartree, Hartree, and Swirles lower state functions and analytic Hartree-Fock upper state functions plus a correction for $r>9.0$. σ^2 (AHF) indicates pure AHF results from Ref. 17.

Transition	σ^2 (HF)	σ^2 (AHF)
O I $2p^4(^3P) \rightarrow 2p^3(^4S)3s(^3S)$	0.103	0.0976
$(^2D)3s(^3D)$	0.112	0.106
$(^2P)3s(^3P)$	0.113	0.108
$(^4S)3d(^3D)$	0.00289	0.00259
$(^2D)3d(^3D)$	0.00326	0.00293
$(^2P)3d(^3D)$	0.00319	0.00288
O II $2p^3(^4S) \rightarrow 2p^2(^3P)3s(^4P)$	0.0678	0.0665
$3d(^4P)$	0.0157	0.0153
$2p^3(^2P) \rightarrow 2p^2(^3P)3s(^2P)$	0.0949	0.0928
N I $2p^3(^4S) \rightarrow 2p^2(^3P)3s(^4P)$	0.142	0.131
$3d(^4P)$	0.00684	0.00599
$2p^3(^2P) \rightarrow 2p^2(^3P)3s(^2P)$	0.196	0.187
$3d(^2P)$	0.0106	0.00963

been obtained from the data listed by Moore.[26] (This procedure was greatly facilitated by a computer code kindly supplied by R. R. Johnston.) In addition to the experimental ν values used for the upper states, ν values obtained from H-F orbital energy parameters[27] were used to compute an additional dipole-integral value for the principal-quantum-number 3 states. This Coulomb approximation to the Hartree-Fock function (after Table 6 of Ref. 1) can provide a moderately direct test of the extent of validity of the CA for these transitions. The directness is obscured somewhat for our purposes because of the deterioration of the $2p$ analytic HF functions at large r. This was noted in Ref. 17 and is evident from Table IV. As a result, the AHF values tend to be somewhat low.

To monitor this situation, we calculated a number of dipole integrals between the HHS lower state functions and Kelly's AHF upper state functions. In addition, a correction was applied for the region $r>9.0$ where the Hartree, Hartree, and Swirles calculations stop, by fitting a CA tail to the H-F integrand. (This only affected the neutral $2p$-$3d$ transitions appreciably—4 to 5 units in the last figure.) These results should be very close to true HF values, and they compare with Kelly's analytic Hartree-Fock results as shown in Table VIII. There is a significant improvement in some, but not all cases.

The results indicate that our approximate results for O I $2p$-$3d$ transitions (Table VI) should be quite good since the result of 2.93×10^{-3} in Table VI for the CA upper state with the HF energy parameter compares quite favorably with the HF result of 2.89×10^{-3} from Table VIII. For the $2p$-$3s$ transitions our approximate result with the HF energy parameter differs by about 33% from the true Hartree-Fock value, this difference now being slightly greater than for the AHF σ^2 value. We have also obtained dipole integrals for the analogous transitions (up to $n=6$) in O II and O III which are not included here.[15]

A few general remarks can be made. For all the $2p$-$3s$ transitions our results are intermediate between the AHF and HFS values, or very close to the AHF result. Thus, our method appears to be superior to the HFS model, but not as good as the AHF since our values with HF orbital energy parameters determining the upper state are not in too good agreement with the HF or AHF values. For the $2p$-$3d$ transitions our results are systematically larger than the AHF. This is partly a real effect due to the better behavior of our functions at large r. It is partly, of course, due to the fact that there is no cancellation in these cases—with one exception—and the $3d$ CA wave functions are too large in the core region[15] (the situation is reversed near the origin, but at distances too close to contribute significantly to σ). Such cases could be improved by employing a cutoff in the integral and thereby excluding an inner segment from the integrand. Since the results are already reasonably good and such an *ad hoc* procedure would destroy the uniformity of the approximation, we choose not to pursue it. The exception mentioned above, for which cancellation occurs in a $2p$-$3d$ transition, appears because the effective quantum number ν of the $3d$ state is greater than 3, and occurs in the O II $2p^3(^2P) \rightarrow 2p^2(^1D)3d\,^2S$ transition. (This cancellation produces a lower value than the AHF result in this one case.) For the $2p$-nd transitions for which $n>4$, our results are likely to be superior to both the HFS and AHF values, owing to the decreasing influence of the core region.

In the case of O II, we have obtained some further results which give quantitative evidence of the effects of

TABLE IX. Radial dipole integrals from the $2p^3(^2P)$ term of O II to the indicated upper states. The effective quantum numbers ν are from experimental term values, and the analytic Hartree-Fock comparison values of σ^2 are from Kelly.[a]

Upper-state parameters ν	Upper-state parameters Term	σ^2 (this calc.) With config. int.	σ^2 (this calc.) Without config. int.	σ^2 (AHF) Without config. int.
2.1559	$(^3P)3s\,^2P$	0.0853	0.0891	0.0928
2.9634	$3d\,^2P$	0.0223	0.0230	0.0206
2.9925	$3d\,^2D$	0.0166	0.0172	0.0146
3.1951	$4s\,^2P$	0.0110	0.0113	
3.9423	$4d\,^2P$	9.09×10^{-3}	9.31×10^{-3}	
3.9897	$4d\,^2D$	6.55×10^{-3}	6.73×10^{-3}	
4.1974	$5s\,^2P$	4.46×10^{-3}	4.55×10^{-3}	
4.9946	$5d\,^2D$	3.02×10^{-3}	3.10×10^{-3}	
2.1323	$(^1D)3s\,^2D$	0.0989	0.103	0.0924
2.9492	$3d\,^2D$	0.0255	0.0262	0.0190
2.9712	$3d\,^2P$	0.0211	0.0218	0.0159
3.0274	$3d\,^2S$	0.0104	0.0108	0.0157
3.1503	$4s\,^2D$	0.0133	0.0136	
3.9180	$4d\,^2D$	9.92×10^{-3}	0.0101	
3.9662	$4d\,^2P$	7.83×10^{-3}	8.03×10^{-3}	
3.9939	$4d\,^2S$	6.31×10^{-3}	6.49×10^{-3}	
4.1592	$5s\,^2D$	4.76×10^{-3}	4.83×10^{-3}	
2.0996	$(^1S)3s\,^2S$	0.119	0.124	0.0935
2.9489	$3d\,^2D$	0.0256	0.0263	0.0165

[a] Reference 17.

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[26] C. E. Moore, Atomic Energy Levels, Natl. Bur. Std. (U. S.), Circ. No. 467 (1949).

[27] P. S. Kelly (private communication).

configuration interaction in transitions of the $2p$-ns and $2p$-nd type. This effect is not large, as was already noted by Hartree, Hartree, and Swirles,[24] but quantitative measures for transition probabilities may prove useful. These results are shown in Table IX, which presents dipole integrals from the $2p^3(^2P)$ term of O II to various upper states for the Hartree-Hartree-Swirles ^2P wave functions with configuration interaction and without configuration interaction, respectively. The available AHF values[17] are included in the table for direct comparison. These latter results do not, of course, include any of the effects of superposition of configurations.

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Hyperfine Structure $^2D_{5/2}$ and $^4F_{9/2}$ States of Ag^{107} and Ag^{109}

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The hfs of the $(4d^95s^2)$ $^2D_{5/2}$ and $(4d^95s5p)$ $^4F_{9/2}$ metastable electronic states in Ag^{107} and Ag^{109} have been measured by the atomic-beam magnetic-resonance method. The results, including the hfs dipole interaction constants which have been corrected for second-order interactions with neighboring fine-structure levels, are as follows:

$$\Delta\nu(\mathrm{Ag}^{109};\, ^2D_{5/2};\, F=3 \leftrightarrow F=2) = 435.4750(15)\ \mathrm{Mc/sec},$$
$$\Delta\nu(\mathrm{Ag}^{107};\, ^2D_{5/2};\, F=3 \leftrightarrow F=2) = 378.8453(3)\ \mathrm{Mc/sec},$$
$$\Delta\nu(\mathrm{Ag}^{109};\, ^4F_{9/2};\, F=5 \leftrightarrow F=4) = 1841.1564(9)\ \mathrm{Mc/sec},$$
$$\Delta\nu(\mathrm{Ag}^{107};\, ^4F_{9/2};\, F=5 \leftrightarrow F=4) = 1596.7506(6)\ \mathrm{Mc/sec},$$
$$A(^2D_{5/2})^{109} = -145.1584(5)\ \mathrm{Mc/sec},\quad A(^2D_{5/2})^{107} = -126.2818(1)\ \mathrm{Mc/sec},$$
$$A(^4F_{9/2})^{109} = -368.214(9)\ \mathrm{Mc/sec},\quad A(^4F_{9/2})^{107} = -319.339(5)\ \mathrm{Mc/sec}.$$

The hfs anomaly for each of the two states is

$$^{107}\Delta^{109}(^2D_{5/2}) = 0.00012(1) \quad \text{and} \quad ^{107}\Delta^{109}(^4F_{9/2}) = -0.00298(3).$$

By comparing the anomaly in the $^2D_{5/2}$ state with that in the ground $^2S_{1/2}$ state, we have obtained the amount of s-state mixing into the $^2D_{5/2}$ state. The contribution to the hfs of the $^4F_{9/2}$ level from each of the individual valence electrons has been estimated. The observed anomaly in the $^4F_{9/2}$ state is in good agreement with the estimated s-electron contribution to the state.

I. INTRODUCTION

THIS is the first in a series of papers devoted to the study of the hfs of several excited metastable electronic levels of the naturally occurring isotopes of the group Ib elements, $\mathrm{Cu}^{63,65}$, $\mathrm{Ag}^{107,109}$, and Au^{197}.[1] The hfs measurements were made by the atomic-beam magnetic-resonance method. Each of the three elements has an $[nd^{10},(n+1)s]^2S_{1/2}$ ground state and each possesses at least one metastable level arising from its $[nd^9,(n+1)s^2]$ configuration and a metastable $^4F_{9/2}$ level arising from its $[nd^9,(n+1)s,(n+1)p]$ configuration. In this paper, we report on the measurements of the hfs separations of the $(4d^95s^2)^2D_{5/2}$ and $(4d^95s5p)^4F_{9/2}$ levels in Ag^{107} and Ag^{109}.

Precision hfs measurements on several levels of an atom are of interest because they frequently provide a good check on the consistency of the interpretations of the results on the individual states. These checks are facilitated by analyzing the various hfs measurements into the contributions from the individual valence electrons. This is the procedure we have followed and, as will be seen below, the results are entirely satisfactory.

II. APPARATUS

The apparatus used in this experiment was essentially the same as that described in detail by Lurio[2]

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* Present location: IBM Research Center, Yorktown Heights, New York.

† Present location: New York University, University Heights, Bronx, New York.

[1] A. G. Blachman and A. Lurio, Bull. Am. Phys. Soc. **8**, 9 (1963); **8**, 351 (1963); D. A. Landman, A. G. Blachman, and A. Lurio, Brookhaven Conference on Molecular and Atomic Resonance, Uppsala, Sweden, 1964 (unpublished).

[2] A. Lurio, Phys. Rev. **126**, 1768 (1962).