

4. Because of the complexity introduced by the stripping process, it is not possible to establish the existence of a term in $\cos^2\theta$ in any of the distributions. In the ground-state neutron distribution, however, it is necessary to assume either that the forward maximum is a result of stripping or that a pronounced $\cos^2\theta$ dependence is present; with the present data the least-squares analysis favors the latter assumption (Table II).

5. In the neutron distributions, the relative contribution resulting from stripping seems to increase with increasing E_x (decreasing Q).

To discuss the compound-nucleus effects, we may assume that B^{11} states are formed by incoming deuterons with orbital angular momentum $l_d=0$ or 1 (we expect that higher values of l_d are improbable by considerations of penetrability). Possible B^{11} states are listed (spin and parity) in Table III, along with values of orbital

angular momentum l' for the outgoing particle corresponding to various possible final states of B^{10} or Be^{10} (listed by spin; parity assumed +). On the basis of penetrability alone, one could account for a relatively low yield to the states $E_x=1.74$ Mev in B^{10} and $E_x=0.0$ Mev in Be^{10} by assuming in agreement with others¹ that these are both states of $J=0$ and that the B^{11} states involved are some combination of $5/2^-$, $3/2^+$, $5/2^+$, and $7/2^+$ or perhaps $3/2^-$ and $7/2^+$. Two B^{11} states of opposite parity are needed to account for the $\cos\theta$ terms on the basis of compound nucleus formation. A model which assumes only the B^{11} states $5/2^-$ and $3/2^+$ is in agreement with these considerations. In addition, it leads to similar angular distributions, with very little $\cos^2\theta$, for states in B^{10} and Be^{10} having spins 1 or 2 and to a more pronounced $\cos^2\theta$ term for states with spin 3 (ground state of B^{10}).

Nuclear Quadrupole Coupling in the Li_2 Molecule*†

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The effect of the quadrupole moment induced in the $1s$ shell on the nuclear quadrupole coupling q in the Li_2 molecule has been investigated for several wave functions. For the most accurate variational wave function of James, the inclusion of the induced moment gives $q/2e = -0.00106a_H^{-3}$. This result, together with the quadrupole coupling $eqQ = +0.060$ Mc/sec for Li^7 , leads to a negative value of the quadrupole moment $Q(Li^7)$. However the value of q is so close to zero that the magnitude and even the sign of Q is uncertain. The value of $1/q$ which determines Q is very sensitive to changes in the molecular wave function, and it is shown that a small modification of the James wave function would lead to a negative $Q(Li^7)$ which agrees in order of magnitude with the prediction of the nuclear shell model. Calculations of q were also carried out for the Heitler-London and Coulson-Duncanson wave functions for the Li_2 molecule.

I. INTRODUCTION

IN a recent investigation of the quadrupole coupling in the Li_2 molecule, Harris and Melkanoff¹ have shown that the sign of the electric field gradient at the Li nucleus is very sensitive to the detailed behavior of the molecular wave function, since the gradient is the difference between the nuclear and the electronic terms which nearly cancel each other. These authors confirm an earlier result of Foley² that the Bartlett-Furry wave function for Li_2 gives a positive quadrupole coupling q which would lead to a positive quadrupole moment Q , in view of the experimental observation³ that eqQ is

positive ($+0.060$ Mc/sec). However, Harris and Melkanoff¹ also carried out a calculation of q with the more accurate variational wave function obtained by James.⁴ The electronic term of q as calculated with this wave function is appreciably larger than for the Bartlett-Furry function; the resultant q is negative, although small. This work does not enable one to draw a definite conclusion about the sign of q , although it shows that a negative sign of q is not excluded. This result is of interest since a positive $Q(Li^7)$ would be hard to understand on the basis of any simple model of the nucleus.^{5,6}

Harris and Melkanoff¹ did not take into account the effect of the quadrupole moment induced⁷ in the $1s$ shell by the nuclear Q . The induced moment around the

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¹ E. G. Harris and M. A. Melkanoff, *Phys. Rev.* **90**, 585 (1953).

² P. Kusch, *Phys. Rev.* **76**, 138 (1949).

³ Logan, Coté, and Kusch, *Phys. Rev.* **86**, 280 (1952).

⁴ H. M. James, *J. Chem. Phys.* **2**, 794 (1934).

⁵ R. D. Present, *Phys. Rev.* **80**, 43 (1950).

⁶ R. Avery and C. H. Blanchard, *Phys. Rev.* **78**, 704 (1950).

⁷ R. M. Sternheimer, *Phys. Rev.* **80**, 102 (1950); **84**, 244 (1951). The latter paper will be referred to as I.

nucleus (A), whose quadrupole coupling is considered, has two effects: (1) it shields the other nucleus (B) and the density connected with the $1s$ shell surrounding it by the amount γ_∞ , where γ_∞ is the ratio of the total induced moment to Q ; (2) it shields the valence electron density by an amount less than γ_∞ which depends on the extent of the penetration of the valence electrons inside the $1s$ shell. The purpose of this paper is to include the effect of the induced moment as calculated from the James and Heitler-London wave functions. For the more accurate James wave function, the inclusion of the induced moment gives $q/2e = -0.00106a_H^{-3}$. The value obtained for the Heitler-London function is $q/2e = 0.00266a_H^{-3}$ as compared to $0.00390a_H^{-3}$ obtained by Harris and Melkanoff.¹ q is smaller by a factor of order $1 - \gamma_\infty = 0.76$ than without shielding. However, not much weight can be given to the positive sign of q as obtained with the Heitler-London function, since this function is presumably much less accurate than that of James. The difference between the Heitler-London and James results arises from the fact that the James electron distribution is concentrated more heavily for small angles θ_A with the internuclear axis at the expense of the large values of θ_A . As a result the value of $\langle (3 \cos^2 \theta_A - 1)/2r_A^3 \rangle$ is greater, increasing the electronic term. If in the actual wave function the electrons are on the average closer to the nucleus than for the James function, $\langle (3 \cos^2 \theta_A - 1)/2r_A^3 \rangle$ will be further increased and q is definitely negative.

Besides the determination of q for Li_2 , a further aim of this paper is to show how the induced moment correction is calculated for the case of molecules, previous calculations⁷ having been restricted to the case of free atoms. It is found that the correction to q can be obtained by simply calculating the interaction of the induced moment with the asymmetric (valence) part of the electronic density in the molecule, in the same way as for atoms.

II. CALCULATION OF THE INDUCED MOMENT

In order to obtain the correction to q for any of the wave functions considered, it is necessary to obtain the moment induced in the $1s$ shell. A complete proof that the correction for q due to the polarizability of the $1s$ shell is accurately given by the induced moment, will be presented in Sec. III.

The induced moment was calculated using the method described in I. For the unperturbed $1s$ function, we took the same function as was used by James:⁴

$$u_0 = (8.82/\sqrt{2})r \exp(-2.69r), \quad (1)$$

where r is the distance from the nucleus and u_0 is r times the $1s$ function normalized according to

$$\int_0^\infty \int_0^\pi u_0^2 dr \times \sin \theta d\theta = 1,$$

where θ is the angle subtended by the radius vector and the axis of the quadrupole moment. The equation to

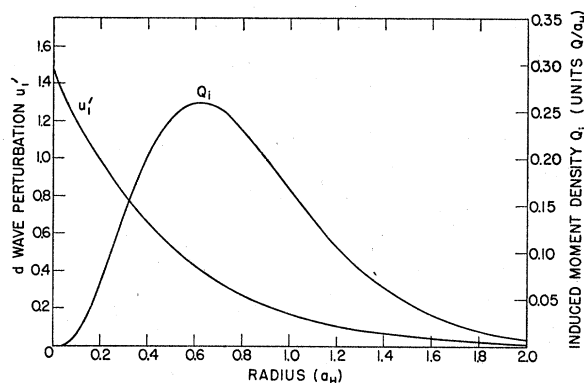


FIG. 1. Induced quadrupole density Q_i and d -wave perturbation u_1' of $1s$ function.

be solved is

$$(H_0 - E_0)u_1 = -H_1u_0, \quad (2)$$

where H_0 and H_1 are the unperturbed and the perturbed part of the Hamiltonian, respectively; u_1 is r times the d wave perturbation. We have

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V_0, \quad (3)$$

$$H_1 = -e^2Q(3 \cos^2\theta - 1)/4r^3, \quad (4)$$

where V_0 is the spherical potential. V_0 was taken as $(-5.38/r)$ Rydbergs in order to be consistent with the wave function, Eq. (1). Similarly the energy $|E_0|$ is taken as $(2.69)^2 = 7.24$ ry. Upon defining the radial functions u_0' and u_1' as in I,

$$u_0 \equiv 2^{-3}u_0'(r), \quad (5)$$

$$u_1 \equiv Qu_1'(r)(3 \cos^2\theta - 1)/2\sqrt{2}, \quad (6)$$

one obtains

$$\left(-\frac{d^2}{dr^2} + \frac{6}{r^2} - \frac{5.38}{r} + 7.24\right)u_1' = \frac{u_0'}{r^3}. \quad (7)$$

Equation (7) can be solved exactly because of the special form of the unperturbed function u_0' which can be written $\kappa r \exp(-Z_0r)$, with $\kappa = 8.82$, $Z_0 = 2.69$. The solution of

$$\left(-\frac{d^2}{dr^2} + \frac{6}{r^2} - \frac{2Z_0}{r} + Z_0^2\right)u_1' = \kappa \exp(-Z_0r)/r^2 \quad (8)$$

can be shown by substitution to be

$$u_1' = \left(\frac{\kappa}{6}\right) \exp(-Z_0r)[1 + (Z_0/3)r]. \quad (9)$$

As shown in I, the induced moment due to both $1s$ electrons, $Q_i(r)dr$ between r and $r+dr$ is given by

$$Q_i dr = (8/5)Qu_0'u_1'r^2 dr. \quad (10)$$

Figure 1 shows u_1' together with Q_i . The total induced

moment

$$Q_{iT} = \int_0^\infty Q_i dr \quad (11)$$

can be obtained by integration using Eqs. (5), (9), and (10):

$$Q_{iT} = Q\kappa^2 / (6Z_0^4). \quad (11a)$$

The value of κ is determined by the requirement

$$\int_0^\infty u_0'^2 dr = \kappa^2 \int_0^\infty r^2 \exp(-2Z_0 r) dr = 1, \quad (12)$$

whence $\kappa = 2Z_0^{3/2}$. Upon inserting this value in (11a) one finds

$$Q_{iT} = 2Q / (3Z_0). \quad (13)$$

For the present case, with $Z_0 = 2.69$, $Q_{iT} = 0.248Q$. It may be noted that the present values of Q_i are quite close to those obtained previously in I (see Table I) using as the unperturbed u_0 the $1s$ function obtained by Fock and Petrashen.⁸ The corresponding value of $|E_{\Delta Q}/E_Q|$ for the atomic $2p$ state (0.166) is somewhat smaller than Q_{iT}/Q because of the penetration of the $2p$ function into the $1s$ shell.

Equation (13) shows that the contribution to the induced moment from the $1s$ shell decreases as Z^{-1} with increasing atomic number Z . However, the number of shells increases with Z ; this effect compensates the decrease for any one shell as given by Eq. (13). This result is consistent with the behavior of the Fermi-Thomas model according to which the total induced moment for the entire atom is independent of Z .

Equation (7) assumes that the perturbing potential is that of the unshielded nuclear moment Q . However, as pointed out in I, the total perturbation includes a contribution from the induced moment. In the present case each $1s$ electron experiences the perturbation due to the moment induced in the other $1s$ state, which amounts to $Q_i/2$. In order to include this effect, one defines

$$\gamma(r) \equiv (1/Q) \left[\int_0^r Q_i dr' + r^5 \int_r^\infty Q_i r'^{-5} dr' \right]; \quad (14)$$

γ is 0 at $r=0$ and (Q_{iT}/Q) for large r .

The equation satisfied by the perturbation upon inclusion of the shielding, is obtained from Eq. (7) by replacing u_0'/r^3 by $(1-\gamma/2)u_0'/r^3$. The resulting equation was solved numerically for the perturbation, say \bar{u}_1' , using the procedure described in I [Eqs. (1)-(12)]. The effect of the $-\gamma/2$ term was found to be very small. The new induced moment \bar{Q}_{iT} calculated with \bar{u}_1' is $0.240Q$, only 3 percent lower than the initial value. The function γ as obtained with the induced moment $\bar{Q}_i \equiv (8/5)Q u_0' \bar{u}_1' r^2$ will be used in the calculation of the quadrupole coupling.

⁸ V. Fock and M. Petrashen, *Physik. Z. Sowjetunion* **8**, 555 (1935).

III. THE QUADRUPOLE COUPLING FOR THE JAMES VARIATIONAL FUNCTION

The variational wave function for the Li_2 ground state obtained by James⁴ is

$$\Psi_J = (1/N_J^{3/2}) \sum_{m n j k} C_{m n j k} (\psi_{m n j k} + \psi_{n m k j}), \quad (15)$$

where the $C_{m n j k}$ are constant coefficients, N_J is a normalization constant and $\psi_{m n j k}$ is the following determinant:

$$\psi_{m n j k} = |(\psi_{1s\alpha})(1)(\psi_{1s\beta})(2)(f_{mj}\alpha)(3) \times (f_{nk}\beta)(4)(\psi_{1s'\alpha})(5)(\psi_{1s'\beta})(6)|, \quad (16)$$

with

$$f_{mj} = \exp(-2\lambda)\lambda^m \mu^j; \quad (17)$$

λ and μ are elliptic coordinates; $\lambda = (r_A + r_B)/R$, $\mu = (r_A - r_B)/R$, where r_A and r_B are the distances from nucleus A and B , respectively, R is the internuclear distance; ψ_{1s} and $\psi_{1s'}$ are $1s$ wave functions centered on nucleus A and B , respectively, whose normalization is $\int \psi_{1s}^2 dV = 1$ ($dV =$ volume element). α and β are the eigenfunctions for spin up and down, respectively. The notation $(\psi_{1s\alpha})(1)$ means that the coordinates of $\psi_{1s\alpha}$ are those of electron 1. In Eq. (16), $\psi_{m n j k}$ is a determinant whose terms include all permutations of electrons 1-6.

Instead of the original wave function obtained by James⁴ which has 18 terms, Harris and Melkanoff¹ used a function composed of 12 terms. It was shown by Melkanoff¹ that the difference in the values of q obtained with the two wave functions is small. Thus, it would not affect the present considerations of the effect of shielding on q . We have used the same function as was used by Harris and Melkanoff, so that the sum in Eq. (15) has 12 terms.

We must first calculate the total electron density ρ_J for the James function. ρ_J is given by

$$\rho_J = 6 \iint |\Psi_J|^2 d\sigma_1 d\tau_{2-6}, \quad (18)$$

where $d\tau_{2-6}$ indicates the space and spin coordinates of electrons 2-6 and σ_1 is the spin of 1. From (16) and (18) one finds for the density ρ_{ff} of the valence electrons,

$$\rho_{ff} = (1/N_J) \sum_{m n j k} \sum_{m' n' j' k'} C_{m n j k} C_{m' n' j' k'} \times [f_{mj} f_{m' j'} I'_{nk, n' k'} + f_{nk} f_{n' k'} I'_{mj, m' j'} + f_{nk} f_{m' j'} I'_{mj, n' k'} + f_{mj} f_{n' k'} I'_{nk, m' j'}], \quad (19)$$

where

$$I'_{mj, nk} \equiv I_{m+n, j+k} - 2J_{mj} J_{nk}, \quad (20)$$

$$I_{m, j} = \int e^{-4\lambda} \lambda^m \mu^j dV, \quad (20a)$$

$$J_{mj} \equiv \int \psi_{1s} e^{-2\lambda} \lambda^m \mu^j dV. \quad (20b)$$

N_J is obtained by integrating $|\Psi_J|^2$ over all coordinates ($d\tau_{1-6}$). One finds

$$N_J = \sum_{mnjk} \sum_{m'n'j'k'} C_{mnjk} C_{m'n'j'k'} [I'_{mj, m'j'} I'_{nk, n'k'} + I'_{nk, m'j'} I'_{mj, n'k'}]. \quad (21)$$

Since ψ_{1s} and f_{mj} are not orthogonal, there are terms in ρ_J of the form $\psi_{1s} f_{mj}$. These terms contribute to the electric field gradient at nucleus A . If ρ_{sf} denotes the part of ρ_J which is linear in ψ_{1s} , one finds

$$\begin{aligned} \rho_{sf} = -(\psi_{1s}/N_J) \sum_{mnjk} \sum_{m'n'j'k'} C_{mnjk} C_{m'n'j'k'} \\ \times \{ f_{mj} [J_{m'j'} I'_{nk, n'k'} + J_{n'k'} I'_{mj, m'j'}] \\ + f_{nk} [J_{n'k'} I'_{mj, m'j'} + J_{m'j'} I'_{mj, n'k'}] \\ + f_{m'j'} [J_{mj} I'_{nk, n'k'} + J_{nk} I'_{mj, n'k'}] \\ + f_{n'k'} [J_{nk} I'_{mj, m'j'} + J_{mj} I'_{nk, m'j'}] \}. \quad (22) \end{aligned}$$

The value of q can be calculated from these expressions and from the value of the net charge concentrated at nucleus B . Because of the non-orthogonality, the coefficient of ψ_{1s}^2 in ρ_J is not exactly 2, and there is also a term linear in ψ_{1s} similar to ρ_{sf} . Upon using Harris's value⁹ for the net charge due to both terms, $-1.973e$, one obtains $+1.027e$ for the charge at B which represents nucleus B and the surrounding $1s$ shell. Instead of the quadrupole coupling q , we will frequently use q' , defined by $q' \equiv q/2e$, so that q' is the average of $(3 \cos^2 \theta_A - 1)/2r_A^3$ over the charge density of the molecule excluding nucleus A .

In order to obtain the shielding effect without ambiguity, it is best to consider this effect as a result of the distortion of the $1s$ shell by the asymmetric potential caused by the other charges. The correction to q is then due to the part of the distortion which behaves as $(3 \cos^2 \theta_A - 1)$. This picture is equivalent to the consideration of the induced moment, as will now be shown.

The distortion of the $1s$ states is caused by the asymmetric part of the potential of the charges other than the $1s$ state being considered. The density of the type ρ_{sf} with spin up (or down) is one-half of the expression given by Eq. (22). Hence, the density ρ' which produces the distortion is

$$\rho' = -\rho_{sf} - \frac{1}{2}\rho_{sf} + \rho_B, \quad (23)$$

where ρ_B is a charge $+1.027$ concentrated at B . Because of the potential produced by ρ' , ψ_{1s} is changed to

$$\tilde{\psi}_{1s} = \psi_{1s} + \psi_p + \psi_d + \dots, \quad (24)$$

where ψ_p and ψ_d are the p and d wave perturbations, respectively. These perturbations can be obtained by solving the Schrödinger equation for the $1s$ function including the potential resulting from ρ' .

The correction to q for the polarizability of the $1s$ shell is obtained by replacing ψ_{1s} by $\tilde{\psi}_{1s}$ in the James

wave function [Eq. (17)]. The most important term of q which arises from this substitution is associated with ψ_{1s}^2 . The ψ_{1s}^2 terms of ρ_J can be written $c\psi_{1s}^2$. Harris has given the value⁹ $c=2.0268$; $c\psi_{1s}^2$ is replaced by $c\tilde{\psi}_{1s}^2$, which includes a term $2c\psi_{1s}\psi_d$. This term is the only one of first order in the perturbation which has the $(3 \cos^2 \theta_A - 1)$ dependence. The contribution to q' is

$$\Delta q' = - \int 2c\psi_{1s}\psi_d(3 \cos^2 \theta_A - 1)/2r_A^3 dV. \quad (25)$$

It can be easily shown that $\Delta q'$ as given by Eq. (25) can be expressed in terms of the function γ associated with the induced moment \tilde{Q}_i :

$$\begin{aligned} \Delta q' = - \int [\gamma(3 \cos^2 \theta_A - 1)/2r_A^3] \\ \times (-\rho_{ff} - \frac{1}{2}\rho_{sf} + \rho_B) dV. \quad (26) \end{aligned}$$

In order to prove Eq. (26), ρ' will be written

$$\rho' = \rho_0 P_0 + \rho_1 P_1 + \rho_2 P_2 + \dots, \quad (27)$$

where $P_l(\theta_A)$ is the Legendre polynomial of order l and the ρ_l are functions of r_A only. The potential produced by ρ_2 is

$$\begin{aligned} V_2 = (8\pi/5) \left[\frac{1}{r^3} \int_0^r \sigma r'^2 dr' + r^2 \int_r^\infty \sigma r'^{-3} dr' \right] P_2 \\ = (8\pi/5) g P_2, \quad (28) \end{aligned}$$

where $\sigma(r') \equiv \rho_2 r'^2$. The function in the square bracket is denoted by g . We note that a factor 2 arises from Rydberg units and a factor $\frac{2}{3}$ from the integration over θ_A . The d wave perturbation \tilde{u}_1 of the $1s$ function is determined by an equation similar to Eq. (4) of I:

$$M\tilde{u}_1 = - (8\pi/5) g P_2 u_0, \quad (29)$$

where M denotes the operator

$$M = -\frac{d^2}{dr^2} + \frac{6}{r^2} + V_0 - E_0. \quad (30)$$

In the present case, $V_0 = -5.38/r$, $E_0 = -7.24$ ry. Here and in the following, the u 's denote r times the corresponding parts of the $1s$ wave function. If we let $u_0 = 2^{-1/2} u_0'$ [see Eq. (5)], \tilde{u}_1 can be written

$$\tilde{u}_1 = (-8\pi/5\sqrt{2}) \tilde{u}_1' P_2, \quad (31)$$

where \tilde{u}_1' satisfies

$$M\tilde{u}_1' = g u_0'. \quad (32)$$

The contribution to q' is given by

$$\Delta q' = -4 \int_0^\pi \int_0^\infty (u_0 \tilde{u}_1 / r^3) P_2 dr \sin \theta d\theta, \quad (33)$$

where the factor 4 arises from the fact that the perturbed density is $2u_0 \tilde{u}_1$ for each $1s$ electron. Upon insert-

⁹ E. G. Harris, thesis, University of Tennessee, 1953 (unpublished).

ing Eq. (31) into (33) one obtains

$$\Delta q' = \frac{32\pi}{25} \int_0^\infty \frac{u_0' \tilde{u}_1'}{r^3} dr. \quad (34)$$

It will be shown that the same expression is obtained, if the quadrupole energy is calculated as the interaction of the induced moment with ρ' . The perturbation u_1 due to the nuclear Q is determined by

$$Mu_1 = QP_2u_0/r^3. \quad (35)$$

Hence, u_1 can be written

$$u_1 = QP_2u_1'/\sqrt{2}, \quad (36)$$

where u_1' satisfies

$$Mu_1' = u_0'/r^3. \quad (37)$$

In view of Eq. (36), the perturbed density due to u_1 is

$$\Delta\rho_{\text{ind}} = 4u_0u_1 = 2Qu_0'u_1'P_2. \quad (38)$$

The potential due to $\Delta\rho_{\text{ind}}$ is

$$V_{\text{ind}} = (8/5)Q \left[\frac{1}{r^3} \int_0^r u_0'u_1'r'^2 dr' + r^2 \int_r^\infty u_0'u_1'r'^{-3} dr' \right] P_2 = (8/5)Qg'P_2, \quad (39)$$

where g' denotes the function in the square bracket. The interaction of V_{ind} with ρ' is given by

$$2\pi \int_0^\infty \int_0^\pi V_{\text{ind}} \rho_2 P_2 r'^2 dr \sin\theta d\theta = (32\pi Q/25) \int_0^\infty g' \sigma dr. \quad (40)$$

Since Eq. (40) equals $\Delta q'Q$, the two expressions for $\Delta q'$, Eqs. (34) and (40) are equivalent, provided that the radial integrals are equal; these integrals will be denoted by \tilde{L} and L , respectively. Using Eq. (37) one finds

$$\begin{aligned} \tilde{L} &= \int_0^\infty (u_0' \tilde{u}_1' / r^3) dr = \int_0^\infty (Mu_1') \tilde{u}_1' dr \\ &= \int_0^\infty u_1' (M\tilde{u}_1') dr, \end{aligned} \quad (41)$$

where the last step follows by partial integration. In view of Eq. (32), Eq. (41) becomes

$$\begin{aligned} \tilde{L} &= \int_0^\infty u_0' u_1' g dr \\ &= \int_0^\infty u_0' u_1' \left[\frac{1}{r^3} \int_0^r \sigma r'^2 dr' + r^2 \int_r^\infty \sigma r'^{-3} dr' \right] dr. \end{aligned} \quad (42)$$

By partial integration \tilde{L} can be transformed to

$$L = \int_0^\infty \sigma \left[\frac{1}{r^3} \int_0^r u_0' u_1' r'^2 dr' + r^2 \int_r^\infty u_0' u_1' r'^{-3} dr' \right] dr, \quad (43)$$

which equals L by virtue of Eqs. (39) and (40). Thus the correction $\Delta q'$ can be calculated as the interaction of the induced moment with the charge outside the 1s shell. The main advantage of this method, as compared to the procedure in which \tilde{u}_1 is calculated, is that the distortion by the nuclear Q can be used with several external distributions without the need of solving a differential equation each time. Moreover, in the present case, u_1 can be obtained analytically, whereas this is not possible for \tilde{u}_1 .

Aside from the term $2c\psi_{1s}\psi_d$, there are other shielding terms which arise from the lack of orthogonality of ψ_{1s} on f_{mj} . These terms arise as follows from the substitution of $\tilde{\psi}_{1s}$ for ψ_{1s} in Eq. (16): (1) there are additional terms in ρ_{sf} caused by the fact that ψ_{1s} in ρ_{sf} [Eq. (22)] should be replaced by $\tilde{\psi}_{1s}$. The perturbation in the density arising from ψ_p is ρ_{pf} , defined as the result of replacing ψ_{1s} by ψ_p in the expression for ρ_{sf} . ψ_p was calculated by solving a differential equation similar to Eq. (29). The contribution to q' due to ρ_{pf} was found to be $\sim 10^{-5} a_H^{-3}$. An even smaller contribution is obtained from ρ_{df} , defined as the result of replacing ψ_{1s} by ψ_d in ρ_{sf} . (2) The J_{mj} [Eq. (20b)] should be calculated using $\tilde{\psi}_{1s}$ instead of ψ_{1s} . This was found to change J_{10} by ~ 0.1 percent and would result in similarly small changes for the other J_{mj} . It can be concluded that the additional shielding terms just described are negligible.

It follows from the preceding discussion that q' is given by

$$\begin{aligned} q' &= - \int (1-\gamma) [(3 \cos^2\theta_A - 1)/2r_A^3] \rho_{ff} dV \\ &\quad - \int (1-\gamma/2) [(3 \cos^2\theta_A - 1)/2r_A^3] \rho_{sf} dV \\ &\quad + [1-\gamma(R)] \int [(3 \cos^2\theta_A - 1)/2r_A^3] \rho_{Bd} dV \\ &\quad + \Delta q'_{\text{exch}}. \end{aligned} \quad (44)$$

The last term in (44) represents a small exchange contribution of the induced moment of the type which has been discussed in I. The expression for $\Delta q'_{\text{exch}}$ and its evaluation, are given in the Appendix.

The integrals in Eq. (44) involving ρ_{ff} and ρ_{sf} will be denoted by A_{ff} and A_{sf} , respectively. A_{ff} and A_{sf} were obtained by a double numerical integration. In this work, the expressions for ρ_{ff} and ρ_{sf} given by Harris⁹ were used. These expressions were also checked by means of Eqs. (19)–(22), using Harris's values⁹ of

the coefficients C_{mijk} . The resulting expressions agree satisfactorily with those of Harris.

ρ_{ff} and ρ_{sf} were evaluated for the internuclear distance $5.63a_H$ for which James⁴ calculated the variational function, instead of the observed $R=5.05a_H$. Therefore, the electronic term of q' will be slightly in error. Harris and Melkanoff¹ have carried out calculations for a Heitler-London wave function for various values of R , from which they showed that for this wave function the electronic part of q' is not sensitive to R . (In the range from $R=4.71a_H$ to $5.50a_H$, this part decreases by only $0.00013a_H^{-3}$.) For the term produced by ρ_B which varies more rapidly with R , the observed distance will be used.

To obtain A_{ff} and A_{sf} , the radial integration was carried out first for 11 angles θ_A . The radial integral for A_{ff} is

$$A_{ff}^{(r)}(\theta_A) = \int_0^\infty (1-\gamma)\rho_{ff}(r_A, \theta_A)/r_A dr_A. \quad (45)$$

Since ρ_{ff} is finite at $r_A=0$, a small region near $r_A=0$ must be excluded. The integral was taken from $r_A=0.2a_H$ to ∞ . It can be easily shown that when the angular integration is carried out for $r_A \leq 0.2a_H$, the contribution from this region to q' is negligible (of the order $10^{-5}a_H^{-3}$). The same considerations apply to A_{sf} . The 11 values of θ_A were taken at intervals of 11.25° for $0^\circ \leq \theta_A \leq 45^\circ$ and at intervals of 22.5° for $\theta_A \geq 45^\circ$.

The results are

$$A_{ff} = 0.00748a_H^{-3}, \quad A_{sf} = -0.00087a_H^{-3}.$$

The term due to ρ_B is given by

$$q_B' = (0.757)(1.027)/R^3 = 0.00603a_H^{-3}. \quad (46)$$

The factor 1.027 is due to the charge $1.027e$ associated with nucleus B and its surrounding $1s$ shell; the factor 0.757 represents the shielding.¹⁰ As shown in the Appendix $\Delta q_{\text{exch}}' = -0.00048a_H^{-3}$ so that the value of q' including shielding is $q_J' = -0.00106a_H^{-3}$.

As a check on the calculations, q' was evaluated without shielding by setting $\gamma=0$ in Eq. (44). The resulting values of the integrals are $A_{ff,0} = 0.00984$, $A_{sf,0} = -0.00096a_H^{-3}$. Here and in the following, the subscript 0 indicates that shielding is not included. The nuclear term is $1.027/R^3 = 0.00797a_H^{-3}$, so that $q_{J,0}' = -0.00091a_H^{-3}$. This value is in very good agreement with that obtained by Harris,⁹ $1/R^3 - 0.00868 = -0.00092a_H^{-3}$. Although the agreement to $10^{-5}a_H^{-3}$ is fortuitous, it indicates that the integration procedure used is adequate.

As was found previously by Harris and Melkanoff,¹ the small value of q_J' makes it impossible to obtain

with certainty the actual sign of the electric field gradient. We note that A_{ff} is reduced by shielding in the ratio 0.760 which is $\approx (1 - Q_{iT}/Q)$. The reason this ratio is obtained is that ρ_{ff} is almost completely external to the $1s$ shell, so that the induced moment has maximum effectiveness in shielding the nucleus. The ρ_{sf} term is reduced by only a factor 0.92. Here the effect of penetration is greater and, in any case, the minimum ratio is $1 - Q_{iT}/2Q = 0.878$. It is seen that the inclusion of shielding does not greatly affect the total value of q_J' for the James wave function, although the individual terms are changed appreciably. The reason is that the important terms of q_J' , namely q_B' and A_{ff} , are reduced by the same factor (≈ 0.76) so that one expects $q_J' \approx 0.76q_{J,0}'$. Since $q_{J,0}'$ is close to zero, the difference $0.24q_{J,0}'$ is very small.

The value of q_J' would give $Q(\text{Li}^2) = -12 \times 10^{-26} \text{ cm}^2$. Interpolation from the curve of quadrupole moments published by Townes, Foley, and Low¹¹ gives $Q(\text{Li}^2) = -1.6 \times 10^{-26} \text{ cm}^2$. It should be emphasized that a relatively small change of the valence density would lead to a value of q' which gives Q of the order of the predictions of the nuclear shell model. Along any line $\theta_A = \text{constant}$, ρ_{ff} increases rapidly with increasing r_A near nucleus A . Because of the factor $1/r_A^3$, the electronic part of q' would be increased considerably if the actual density would rise faster near A than ρ_J . Thus, if the valence density ρ_{ff} were changed to a density $\bar{\rho}_{ff}$ such that¹² $\bar{\rho}_{ff}(r_A, \theta_A) = 1.2^3 \rho_{ff}(1.2r_A, \theta_A)$, A_{ff} would be increased to $1.2^3 A_{ff}$ and q' would be $-0.0065a_H^{-3}$ leading to $Q = -2.0 \times 10^{-26} \text{ cm}^2$. Moreover, A_{ff} is very sensitive to changes of the angular dependence of the density. If ρ_{ff} is increased by a factor 1.15 at $\theta_A = 0^\circ$, 1.10 at 22.5° , 1.05 at 45° , and decreased by a factor 0.80 for $\theta_A \geq 90^\circ$ (to ensure normalization), q' becomes $-0.00354a_H^{-3}$, so that $Q = -3.6 \times 10^{-26} \text{ cm}^2$. If the actual valence density should be both more internal and more peaked near the internuclear axis, in the manner just described, one finds $q' = -0.0107a_H^{-3}$ leading to $Q = -1.2 \times 10^{-26} \text{ cm}^2$. These considerations show that, although the value of q' obtained from the James wave function is unlikely, it is quite possible that the James wave function is still accurate enough for many purposes, since a small change of the wave function results in a considerable change of $1/q'$.

IV. THE QUADRUPOLE COUPLING FOR THE HEITLER-LONDON AND COULSON-DUNCANSON WAVE FUNCTIONS

The calculation of the shielding effect has been carried out for the Heitler-London wave function for Li_2 discussed by James.⁴ This function has also been considered by Harris and Melkanoff¹ and is given by

$$\Psi_{HL} = (1/N_{HL}^{1/2})(\psi_{ab} + \psi_{ba}), \quad (47)$$

¹⁰ The factor 0.757 rather than 0.760 is used because the $1s$ term of ρ_J is $2.027\psi_{1s}^2$, so that the induced moment is increased to $(0.240) \times (2.027/2)Q$.

¹¹ Townes, Foley, and Low, Phys. Rev. **76**, 1415 (1949).

¹² The factor 1.2^3 is required for normalization.

where N_{HL} is a normalization factor, ψ_{ab} is the determinant

$$\psi_{ab} = |(\psi_{1s\alpha})(1)(\psi_{1s\beta})(2)(a\alpha)(3)(b\beta)(4) \\ \times (\psi_{1s'\alpha})(5)(\psi_{1s'\beta})(6)|, \quad (48)$$

and ψ_{ba} differs from ψ_{ab} by the interchange of a and b . Here,

$$a \equiv nr_A \exp(-0.65r_A), \quad (49)$$

$$b \equiv nr_B \exp(-0.65r_B), \quad (50)$$

are valence functions centered on nuclei A and B , respectively; n is a normalization constant to be determined below. In Eq. (48) the determinant includes all permutations of electrons 1-6.

The expressions for the density for the James wave function can be used here. Equation (47) corresponds to a single term of Ψ_J in Eq. (15) with f_{mj} and f_{nk} replaced by a and b , respectively. The valence density is given by

$$\rho_v = (1/N_{HL})[a^2 I_{bb} + b^2 I_{aa} + 2ab I_{ab}], \quad (51)$$

where

$$I_{aa} = I_{bb} = N_1 - J_a^2 - J_b^2,$$

$$I_{ab} = N_2 - 2J_a J_b,$$

$$N_1 = \int a^2 dV, \quad N_2 = \int ab dV, \quad (51a)$$

$$J_a = \int \psi_{1s} a dV, \quad J_b = \int \psi_{1s} b dV.$$

By integrating over all coordinates one finds that N_{HL} is given by

$$N_{HL} = I_{aa}^2 + I_{ab}^2. \quad (52)$$

Similarly to Eq. (22), one obtains for the density due to the overlap of ψ_{1s} with the valence functions,

$$\rho_{sv} = - (2\psi_{1s}/N_{HL}) \{ a [J_a I_{bb} + J_b I_{ab}] \\ + b [J_b I_{aa} + J_a I_{ab}] \}. \quad (53)$$

The 1s density surrounding nucleus A is given by

$$\rho_{ss} = (\psi_{1s}^2/N_{HL}) [I_{aa}(N_1 + I_{aa}) + I_{ab}(N_2 + I_{ab})]. \quad (54)$$

The constant n in (49) and (50) was so chosen that $N_1^2 + N_2^2 = 1$. In order to obtain n , we note that a value $n = 0.111$ would give $N_1 = 1$ from Eq. (51a). With this normalization one obtains $N_2 = 0.586$ by analytic integration. Hence

$$n = 0.111 [1 + (0.586)^2]^{-1/2} = 0.103. \quad (55)$$

The resulting values of the integrals are: $N_1 = 0.863$, $N_2 = 0.506$, $I_{aa} = 0.835$, $I_{ab} = 0.487$, $J_a = 0.156$, $J_b = 0.0625$. In all of these calculations the actual $R = 5.05a_H$ is used. With these values of the constants, the electronic density is

$$\rho_{HL} = 2.035\psi_{1s}^2 - 0.342\psi_{1s}a - 0.273\psi_{1s}b \\ + 0.894(a^2 + b^2) + 1.042ab - 0.342\psi_{1s}'b \\ - 0.273\psi_{1s}'a + 2.035\psi_{1s}'^2, \quad (56)$$

where ψ_{1s}' is the 1s function centered on B . The quadrupole coupling is given by

$$q' = -0.894 \int (1-\gamma) [(3 \cos^2\theta_A - 1)/2r_A^3] b^2 dV \\ - 1.042 \int (1-\gamma) [(3 \cos^2\theta_A - 1)/2r_A^3] ab dV \\ + 0.273 \int (1-\gamma/2) [(3 \cos^2\theta_A - 1)/2r_A^3] \psi_{1s} b dV \\ + 0.756e_B/R^3. \quad (57)$$

The integrals appearing in q' will be denoted by A_{bb} , A_{ab} , and $A_{1s,b}$, respectively; in the last term, e_B is the effective charge associated with nucleus B and its surrounding 1s shell. It is given by

$$e_B = 3 - 2.035 + 0.342J_a + 0.273J_b = 1.035. \quad (58)$$

A_{bb} , A_{ab} , and $A_{1s,b}$ were evaluated by the same procedure as the A 's of the James function. However, for the angles $\theta_A < 45^\circ$ an interval of 5.63° , rather than 11.25° , was used because the A 's have a fairly pronounced variation in this region. The reason is that the closest distance of the line $\theta_A = 11.25^\circ$ to nucleus B is $\sim a_H$, and $b(r_B)$ has a maximum at $r_B = 1/0.65 = 1.54a_H$. As a result, the radial integral $A_{bb}^{(r)}$

$$A_{bb}^{(r)}(\theta_A) = \int_{\delta}^{\infty} b^2(r_A, \theta_A)/r_A dr_A, \quad (59)$$

has a maximum at $\theta_A \approx 11.25^\circ$; here δ is a small radius introduced to give a convergent integral. A similar result holds for the integral over ab . The results of the integration are: $A_{bb} = 0.00276a_H^{-3}$, $A_{ab} = 0.00123a_H^{-3}$, $A_{1s,b} = 0.00121a_H^{-3}$. The resulting value of q_{HL}' as obtained from Eqs. (57) and (58) is $q_{HL}' = 0.00266a_H^{-3}$.

In order to check the numerical integrations, the value of q' without shielding was also calculated. By setting $\gamma = 0$ in Eq. (57), one finds $A_{bb,0} = 0.00357$, $A_{ab,0} = 0.00159$, and $A_{1s,b,0} = 0.00128a_H^{-3}$. These values of the A 's are in satisfactory agreement with those of Harris and Melkanoff,^{1,9} who obtain 0.00350, 0.00154, and 0.00141, respectively. The resulting value of q' is $q_{HL,0}' = 0.00354a_H^{-3}$.

The fact that q_{HL}' is positive cannot be given too much weight because the Heitler-London function is only very approximate. The reason for the difference of the signs of q_{HL}' and q_J' is that the electronic part of q' , q_{el}' , is smaller for the Heitler-London function. By plotting both ρ_J and ρ_{HL} as a function of r_A for various θ_A , it was found that part of the difference of the q_{el}' arises from the fact that ρ_J is more peaked around $\theta_A = 0^\circ$ than ρ_{HL} .

The value of q' obtained with the Bartlett-Furry¹³ function, q_{BF}' , can be obtained from the preceding

¹³ J. H. Bartlett, Jr., and W. H. Furry, Phys. Rev. 38, 1615 (1931).

results by setting $J_a = J_b = 0$. This procedure corresponds to the fact that the Bartlett-Furry function does not include the inner shells. One thus finds

$$q_{BF}' = 0.760/R^3 - N_1 A_{bb} - 2N_2 A_{ab} = 0.00227 a_H^{-3}. \quad (60)$$

Coulson and Duncanson¹⁴ have obtained a molecular orbital type wave function for the Li_2 molecule in which the state of the valence electrons is represented by

$$\Psi_{CD} = (2N_{CD})^{-\frac{1}{2}} [\psi_{2sA}(1) + \psi_{2sB}(1)] \times [\psi_{2sA}(2) + \psi_{2sB}(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)], \quad (61)$$

where N_{CD} is a normalization constant and ψ_{2sA} is a $2s$ function centered on A , which is given by

$$\psi_{2sA} = n_{CD} (r_A - 1.01) \exp(-0.81 r_A), \quad (62)$$

ψ_{2sB} is obtained from ψ_{2sA} by replacing r_A by r_B ; n_{CD} is a normalization constant chosen as $n_{CD} = 0.301$, so that $\int \psi_{2sA}^2 dV = 1$. By analytic integration¹⁵ one finds

$$\int \psi_{2sA} \psi_{2sB} dV = 0.506, \quad (63)$$

so that $N_{CD} = 1.506$. Because $(\psi_{2sA} + \psi_{2sB})$ is orthogonal on ψ_{1s} , no cross terms involving ψ_{1s} appear in q' which is given by

$$q_{CD}' = 0.760/R^3 - (1/N_{CD}) \times \left\{ \int (1-\gamma) [(3 \cos^2 \theta_A - 1)/2r_A^3] \psi_{2sB}^2 dV + 2 \int (1-\gamma) [(3 \cos^2 \theta_A - 1)/2r_A^3] \psi_{2sA} \psi_{2sB} dV \right\}. \quad (64)$$

By numerical integration, the integrals appearing in (64) were found to have the values 0.00367 and 0.00127 a_H^{-3} , respectively. The result for q' is

$$q_{CD}' = 0.760/R^3 - 0.00412 = 0.00178 a_H^{-3}. \quad (65)$$

Concerning the positive sign of q_{CD}' , the same remark applies as for the Heitler-London result.

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APPENDIX. EFFECT OF EXCHANGE ON THE SHIELDING CORRECTION

The exchange contribution to the shielding correction⁷ arises from the fact that the field acting on the $1s$ electrons includes a term arising from the overlap of $1s$ with the valence wave function with parallel spin. The perturbation of the $1s$ function caused by this field contributes to q' . The same treatment as was given above [Eqs. (26)–(43)] shows that the change of q'

¹⁴ C. A. Coulson and W. E. Duncanson, Proc. Roy. Soc. (London) **A181**, 378 (1943).

¹⁵ C. A. Coulson, Proc. Cambridge Phil. Soc. **38**, 210 (1942).

can be calculated from the perturbation u_1 of the $1s$ function by the nuclear Q . The overlap of u_1 with the valence function produces a term $Q\Delta q_{\text{exch}}'$ in the electrostatic energy from which $\Delta q_{\text{exch}}'$ is obtained.

If one would use the actual James wave function for the valence electrons, the calculation of $\Delta q_{\text{exch}}'$ would be very complicated. However, since the effect is quite small we make the approximation of replacing Ψ_J by the following wave function for the valence electrons

$$\Phi_v(1, 2) = \phi_v(1)\phi_v(2), \quad (A1)$$

where

$$\phi_v = (\rho_{ff}/2)^{\frac{1}{2}}. \quad (A2)$$

Here ρ_{ff} and ϕ_v are regarded as functions of r_A and θ_A . Φ_v is a product wave function which gives the same valence density as the James function. The use of Φ_v is not expected to introduce any serious error and should give the correct order of magnitude of the exchange effect.

ϕ_v , as defined by Eq. (A2), is a superposition of s , p , d , f , \dots waves centered at A . We write

$$\phi_v = \phi_s \Theta_0 + \phi_p \Theta_1 + \phi_d \Theta_2 + \dots, \quad (A3)$$

where $\Theta_l = [(2l+1)/2]^{\frac{1}{2}} P_l$. ϕ_s , ϕ_p , and ϕ_d are, respectively, the radial s , p , and d , functions, and are obtained from

$$\phi_{s,p,d}(r_A) = \int_0^\pi \phi_v \Theta_{0,1,2} \sin \theta_A d\theta_A, \quad (A4)$$

where the subscripts 0, 1, 2 correspond to s , p , d , respectively. The f and higher terms of ϕ_v make a negligible contribution to the exchange effect and will be disregarded. ϕ_s , ϕ_p , and ϕ_d were obtained by numerical integration for about 10 radii in the interval $0 \leq r_A \leq 3a_H$. For larger r_A , ψ_{1s} and u_1' are very small, so that the overlap with ϕ_v can be neglected.

It is convenient to use functions normalized to a volume element $r_A^2 dr_A \sin \theta_A d\theta_A$. We write

$$\phi_v' \equiv (2\pi)^{\frac{1}{2}} \phi_v \equiv (v_s \Theta_0 + v_p \Theta_1 + v_d \Theta_2)/r_A, \quad (A5)$$

so that v_s , v_p , and v_d are $(2\pi)^{\frac{1}{2}} r_A$ times ϕ_s , ϕ_p , and ϕ_d , respectively.

Consider the exchange of $\phi_v'(1)$ with the $1s$ electron of parallel spin which will be labeled $i=3$. The corresponding electron density is

$$\rho_{13} = \frac{1}{2} \left\{ \frac{u_0'}{\sqrt{2r}} + \frac{Q u_1' P_2}{\sqrt{2r}} \right\}^2 (1) \phi_v'^2(3) + \frac{1}{2} \left\{ \frac{u_0'}{\sqrt{2r}} + \frac{Q u_1' P_2}{\sqrt{2r}} \right\}^2 (3) \phi_v'^2(1) - \left\{ \left[\frac{u_0'}{\sqrt{2r}} + \frac{Q u_1' P_2}{\sqrt{2r}} \right] \phi_v' \right\} (1) \times \left\{ \left[\frac{u_0'}{\sqrt{2r}} + \frac{Q u_1' P_2}{\sqrt{2r}} \right] \phi_v' \right\} (3). \quad (A6)$$

The last term gives the exchange effect. Upon using Eq. (A5) for ϕ_s' this term becomes

$$\rho_{\text{exch}} = - \left\{ \left[\frac{u_0'}{\sqrt{2}r} + \frac{Qu_1'P_2}{\sqrt{2}r} \right] \left[\frac{v_s\Theta_0 + v_p\Theta_1 + v_d\Theta_2}{r} \right] \right\} (1)$$

$$\times \left\{ \left[\frac{u_0'}{\sqrt{2}r} + \frac{Qu_1'P_2}{\sqrt{2}r} \right] \left[\frac{v_s\Theta_0 + v_p\Theta_1 + v_d\Theta_2}{r} \right] \right\} (3). \quad (\text{A7})$$

ρ_{exch} gives rise to the following terms ΔE_i in the electrostatic energy: (1) ΔE_1 arising from the P_0 part of the potential of the density $\sim (Qu_1'v_dP_2\Theta_2)(1)$ acting on the term $\sim (u_0'v_s\Theta_0)(3)$; (2) ΔE_2 arising from the P_1 potential of $(Qu_1'P_2v_p\Theta_1)(1)$ acting on $(u_0'v_p\Theta_1)(3)$; (3) ΔE_3 arising from the P_2 potential of $(Qu_1'P_2v_s\Theta_0)(1)$ acting on $(u_0'v_d\Theta_2)(3)$; (4) ΔE_4 arising from the P_2 potential of $(Qu_1'P_2v_d\Theta_2)(1)$ acting on $(u_0'v_s\Theta_0)(3)$. In addition, there are four terms which are obtained from the preceding by interchanging electrons 1 and 3.

In order to obtain ΔE_1 one writes the density with the coordinates (1),

$$\rho_1(1) = - (2^{-\frac{1}{2}} Qu_1'v_dP_2\Theta_2/r^2)(1). \quad (\text{A8})$$

The relevant term in the potential $2/r_{13}$ is $2P_0(1)P_0(3)/r_>$, where $r_>$ is the greater of r_1 and r_3 . The potential due to $\rho_1(1)$ is

$$V_1(3) = -2^{\frac{1}{2}} Q \left[\frac{1}{r_3} \int_0^{r_3} u_1'v_d dr_1 + \int_{r_3}^{\infty} u_1'v_d r_1^{-1} dr_1 \right]$$

$$\times \left(\int_0^\pi P_2\Theta_2 \sin\theta_1 d\theta_1 \right) P_0(3)$$

$$= - (2/5^{\frac{1}{2}}) Q V_1'(r_3) P_0(3), \quad (\text{A9})$$

where V_1' is the function in the square bracket; r_i and θ_i denote r and θ for electron i . $V_1(3)$ acts on the following density

$$\rho_1'(3) = 2^{-\frac{1}{2}} u_0'v_s\Theta_0/r_3^2. \quad (\text{A10})$$

This gives

$$\Delta E_1 = \int_0^\pi \int_0^\infty V_1(3) \rho_1'(3) r_3^2 dr_3 \sin\theta_3 d\theta_3$$

$$= - (2/5^{\frac{1}{2}}) \int_0^\infty V_1' u_0'v_s dr_3. \quad (\text{A11})$$

Equation (A7) shows that ρ_{exch} has a term $\rho_1'(1)\rho_1(3)$ which gives the same electrostatic energy as $\rho_1(1)\rho_1'(3)$. The contribution to $\Delta q_{\text{exch}}'$ from both terms is

$$\Delta q_1' = 2\Delta E_1/Q = - (4/5^{\frac{1}{2}}) \int_0^\infty V_1' u_0'v_s dr_3. \quad (\text{A12})$$

The contributions $\Delta q_i'$ of the other terms $2\Delta E_i$ can be found in the same manner as $\Delta q_1'$. The results are as follows:

$$\Delta q_2' = - (8/15) \int_0^\infty V_2' u_0'v_p dr, \quad (\text{A13})$$

where

$$V_2'(r) = (1/r^2) \int_0^r u_1'v_p r' dr' + r \int_r^\infty u_1'v_p r'^{-2} dr', \quad (\text{A14})$$

$$\Delta q_3' = - (4/5^{\frac{1}{2}}) \int_0^\infty V_3' u_0'v_d dr, \quad (\text{A15})$$

$$V_3'(r) = r^{-3} \int_0^r u_1'v_s r'^2 dr' + r^2 \int_r^\infty u_1'v_s r'^{-3} dr'. \quad (\text{A16})$$

$$\Delta q_4' = - (8/35) \int_0^\infty V_4' u_0'v_d dr, \quad (\text{A17})$$

$$V_4'(r) = r^{-3} \int_0^r u_1'v_d r'^2 dr' + r^2 \int_r^\infty u_1'v_d r'^{-3} dr'. \quad (\text{A18})$$

If the integrals appearing in Eqs. (A12), (A13), (A15), and (A17) are denoted by K_1 , K_2 , K_3 , and K_4 , respectively, $\Delta q_{\text{exch}}'$ can be written

$$\Delta q_{\text{exch}}' = -2 \left[(4/5^{\frac{1}{2}}) K_1 + (8/15) K_2 \right. \\ \left. + (4/5^{\frac{1}{2}}) K_3 + (8/35) K_4 \right], \quad (\text{A19})$$

where the factor 2 takes into account that both valence electrons contribute to the exchange.

The K_i were evaluated by numerical integration over v_s , v_p , and v_d . The values are: $K_1 = 11.66 \times 10^{-5}$, $K_2 = 1.87 \times 10^{-5}$, $K_3 = 5.73 \times 10^{-5}$, $K_4 = 0.25 \times 10^{-5}$, so that $\Delta q_{\text{exch}}' = -0.00048 a_{\text{H}}^{-3}$.