INTERACTION OF SIGMA AND PIELECTRONS IN THE FREE-ELECTRON MODEL II. REVISED INTEGRALS FOR THREE DIMENSIONS

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The formulae for the electron-electron and the electron-core interaction have been thoroughly studied for the three-dimensional free-electron model of linear systems, and the errors of an earlier approach have been removed. For the electron-electron integrals all kinds of the interaction, sigma-sigma, pi-pi and pi-sigma, have been examined. The formulae useful for the forthcoming treatment of the interaction problem in the free-electron model with the radius of the potential box tending to zero have been outlined.

1. Introduction

In [1], henceforth denoted as Part I, we presented a scheme by which a system of π and σ electrons can be quantized in a linear unsaturated molecule. The molecule is represented by a cylindrical potential box extended along the path of the CC-bonds. We assume the box corresponds to a straightened chain of the linear molecule, *i. e.* the angles between the bonds are all equal 180°. Both π and σ have a free-electron character, hence, the one-electron wave functions are those of Eq. (1) of Part I and the corresponding energies are given in Eq. (2) of Part I. The number q equals 1 in all cases and may be omitted.

The total wave function of the system is an antisymmetrized product of the one-electron wave functions. The fundamental electron-electron interaction integrals are the Coulomb and the exchange ones. The Coulomb integral is given explicitly in Eq. (5) of Part I, where the denominator of the integrand, denoting the distance between two electrons, should be written correctly as $|\boldsymbol{r}-\boldsymbol{r}'|$.

In Part I we omitted some terms which, though they vanish for the case of different quantum parameters, cannot be rejected when these parameters are equal. Also minor errors have been made, so the general purpose of this, and the forthcoming paper (Part III), is to reconsider the electron-electron interaction in the FE model correctly and more

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fully than before. In particular, we shall: (*i*) remove the defects of Part I and Ref. [2], (*ii*) clarify the problem of convergence raised recently in [3] for the interaction integrals in the case when R, the radius of the potential box, tends to zero, and (*iii*) examine — for the same case as in (*ii*) — the nature of simplifications made in our former calculations on the electron-electron interaction. The effect of the corrected scheme on the electron excitation energies of ethylene, butadiene, and long polyene and polymethine chains will be also considered. In the present paper we calculate thoroughly the integrals for the three-dimensional free-electron model.

2. *Electron-electron interaction integrals*

2.1. Basic formulae

In general, the FE Coulomb and exchange integrals are

$$J_{nm}^{ll'} = \frac{e^2}{L}(I_{0,0}^{ll'} + I_{2n,2m}^{ll'} - I_{0,2n}^{ll'} - I_{0,2m}^{ll'})^{\text{Coul}} \tag{1}$$

and

$$K_{nm}^{ll'} = \frac{e^2}{L}(I_{n+m,n+m}^{ll'} + I_{n-m,n-m}^{ll'} - 2I_{n+m,n-m}^{ll'})^{\text{exch}} \tag{2}$$

where e is the electron charge, L the length of the potential box, and l and l' have the same meaning as in Part I.

The general form of I is:

$$I_{s,t}^{ll'(\text{Coul,exch})} \equiv I_{c,a}^{ll'(\text{Coul,exch})} =$$

$$= L^{-1}\int d\tau \int d\tau' \frac{\cos cz \cos az'}{|\mathbf{r}-\mathbf{r}'|} F_{ll'}(r, r')D_{ll'}(\vartheta, \vartheta') \tag{3}$$

where

$$F_{ll'}(r, r') = Q_l^2 Q_{l'}^2 J_l(u_l r)J_{l'}(u_{l'} r') \begin{bmatrix} J_l(u_l r)J_{l'}(u_{l'} r') \\ \text{or} \\ J_{l'}(u_{l'} r)J_l(u_l r') \end{bmatrix} \tag{4}$$

$$D_{ll}(\vartheta, \vartheta') = T_l^2 T_{l'}^2 \cos l\vartheta \cos l'\vartheta' \begin{bmatrix} \cos l\vartheta \cos l'\vartheta' \\ \text{or} \\ \cos l'\vartheta \cos l\vartheta' \end{bmatrix}. \tag{5}$$

Symbols c and a are the transforms of the integer quantum parameters s and t:

$$c = s\pi L^{-1}, \qquad a = t\pi L^{-1} \tag{6}$$

and

$$d\tau = r dr d\vartheta dz, \qquad d\tau' = r' dr' d\vartheta' dz' \tag{7}$$

$$0 \leqslant z, z' \leqslant L, \quad 0 \leqslant r, r' \leqslant R, \quad 0 \leqslant \vartheta, \vartheta' \leqslant 2\pi. \tag{7a}$$

The upper expressions in (4) and (5) are valid for the Coulomb integral, the lower for the exchange integral; $u_l R$ and $u_{l'} R$ are the constants equal to the arguments for which the Bessel functions J of orders l and l' attain the first zeros. For the σ electrons l and l' is zero, whereas for the π electrons these indices are unity. Symbols Q and T denote the normalization coefficients; we have [4]

$$Q_0 = 2.724 \cdot R^{-1}, \qquad Q_1 = 3.514 \cdot R^{-1} \tag{8}$$

and

$$T_0 = (2\pi)^{-\frac{1}{2}}, \qquad T_1 = \pi^{-\frac{1}{2}}. \tag{9}$$

Let us note that (3) does not change when the sequence of s and t and/or that of l and l' are interchanged. For $l = l'$ we have

$$I_{s,t}^{ll(\mathrm{Coul})} = I_{s,t}^{ll(\mathrm{exch})}. \tag{3a}$$

The same concerns the components of I in the subsequent section.

The mixing of configurations for the operator of the electron-electron interaction provides the integrals which can be calculated in a way similar to that applied for J and K.

2.2. Integral for $s \neq t$

We substitute in Eq. (3)

$$(|\boldsymbol{r}-\boldsymbol{r}'|)^{-1} = \sum_{m=0}^{\infty} \varepsilon_m \cos[m(\vartheta-\vartheta')] \int_0^{\infty} dk J_m(kr) J_m(kr') e^{-k|z-z'|}, \tag{10}$$

where $\varepsilon_0 = 1$ and $\varepsilon_m = 2$ for $m = 1, 2, 3 \ldots$, *etc.*; see [5]. In the case of the $\sigma-\sigma$ interaction ($l = l' = 0$) the effect of (10) is equivalent to that of the Green function of Eq. (12), Part I, multiplied by the factor 8π. The sequence of the integration over k can be interchanged with that over z and z'. This is permissible because the uniform convergence of (10) with respect to the variables z and z' exists in the whole interval $0 \leqslant z, z' \leqslant L$. In fact, (*i*) the integral $\int_0^{\infty} dk\, J_m(kr)\, J_m(kr')$ is convergent for any integer $m \geqslant 0$; (*ii*) the function $f(k, z, z') = \exp(-k|z-z'|)$ is a non-increasing function of k for any z and z' in the interval $0 \leqslant z, z' \leqslant L$; (*iii*) for $k = 0$ the function $f(k, z, z')$ is smaller than a constant $C(> 1)$ which is independent of z and z'. Hence, the conditions of the Abel criterion for the uniform convergence of the integral (10) are fulfilled (see [6], Appendix II). By performing in (3) the integration over z and z' we obtain

$$I_{s,t}^{ll'(\mathrm{Coul,exch})} = A_{s,t}^{ll'(\mathrm{Coul,exch})} + B_{s,t}^{ll'(\mathrm{Coul,exch})} \tag{11}$$

where

$$A_{s,t}^{ll'(\mathrm{Coul,exch})} = -L^{-1} \int_0^R r dr \int_0^{2\pi} d\vartheta \int_0^R r' dr' \int_0^{2\pi} d\vartheta' F_{ll'}(r, r') D_{ll'}(\vartheta, \vartheta') \times$$

$$\times \sum_{m=0}^{\infty} \varepsilon_m \cos[m(\vartheta-\vartheta')] \int_0^{\infty} J_m(kr) J_m(kr') dk \times$$

$$\times \left\{ \frac{k^2}{(c^2+k^2)(a^2+k^2)} \left[\cos^2 (c+a) \frac{L}{2} + \cos^2 (c-a) \frac{L}{2} \right] + \right.$$

$$+ \frac{ac}{(c^2+k^2)(a^2+k^2)} \left[\cos^2 (c+a) \frac{L}{2} - \cos^2 (c-a) \frac{L}{2} \right] -$$

$$\left. - \exp(-Lk)(\cos cL + \cos aL) \left[\frac{c^2}{c^2-a^2} \frac{1}{c^2+k^2} - \frac{a^2}{c^2-a^2} \frac{1}{a^2+k^2} \right] \right\}, \tag{12}$$

and

$$B_{s,t}^{ll'(\text{Coul,exch})} = L^{-1} \int_0^R rdr \int_0^{2\pi} d\vartheta \int_0^R r'dr' \int_0^{2\pi} d\vartheta' F_{ll'}(r, r') D_{ll'}(\vartheta, \vartheta') \times$$

$$\times \sum_{m=0}^{\infty} \varepsilon_m \cos [m(\vartheta - \vartheta')] \int_0^{\infty} J_m(kr) J_m(kr') dk \times$$

$$\times \left\{ \frac{1}{2} \left[\frac{\sin (c+a)L}{c+a} + \frac{\sin (c-a)L}{c-a} \right] \left(\frac{1}{c^2+k^2} + \frac{1}{a^2+k^2} \right) - \right.$$

$$\left. - \frac{e^{-Lk}}{(c^2+k^2)(a^2+k^2)} (c \sin cL + a \sin aL) \right\} k. \tag{13}$$

In both terms the integration over k can be performed, getting convergent results. Let us start with the term A. The contents of the second square brackets in (12) is $(-1) \sin cL \sin aL$, thus — due to (6) — it vanishes for any c and a also in the case of $c = a$; for the case of $c = a = 0$ see Section 2.4. The remaining terms in (12) can be integrated with the aid of the formula [5]

$$J_0(k\tilde{\omega}) = \sum_{m=0}^{\infty} \varepsilon_m \cos [m(\vartheta - \vartheta')] J_m(kr) J_m(kr') \tag{14}$$

where

$$\tilde{\omega} = [r^2 + r'^2 - 2rr' \cos (\vartheta - \vartheta')]^{1/2}. \tag{15}$$

If (14) is substituted in (12), the non-vanishing terms in (12) give the integrals of the type

$$\int_0^{\infty} dk \frac{J_0(k\tilde{\omega})}{b^2+k^2} = \frac{\pi}{2b} [I_0(b\tilde{\omega}) - \boldsymbol{L}_0(b\tilde{\omega})] \tag{16}$$

(see [6]) and

$$\int_0^{\infty} dk \frac{e^{-Lk} J_0(k\tilde{\omega})}{b^2+k^2} =$$

$$= \left\{ \frac{\sin bL}{b} \operatorname{Ci}(bL) + \frac{\cos bL}{b} \left[\frac{\pi}{2} - \operatorname{Si}(bL) \right] \right\} I_0(b\tilde{\omega}) + M(b\tilde{\omega}), \tag{17}$$

where

$$I_m(b\tilde{\omega}) = \sum_{\nu=0}^{\infty} \frac{(\frac{1}{2} b\tilde{\omega})^{m+2\nu}}{\nu!\Gamma(m+\nu+1} \tag{18}$$

is the Bessel function of the second kind;

$$\boldsymbol{L}_m(b\tilde{\omega}) = \sum_{\nu=0}^{\infty} \frac{(\frac{1}{2} b\tilde{\omega})^{m+2\nu+1}}{\Gamma(\nu+3/2)\Gamma(m+\nu+3/2)} \tag{19}$$

is the Struve function of the second kind [6], and

$$M(b\tilde{\omega}) = b^{-1} \sum_{m=1}^{m=\infty} \sum_{n=m}^{n=\infty} (-1)^m \frac{[2(m-1)]!}{(bL)^{2m-1}} \left(\frac{b\tilde{\omega}}{2}\right)^{2n} (n!)^{-2}. \tag{20}$$

The term-by-term integration performed in (17) was permissible in view of the uniform convergence of the integrated series. Equations (12)–(17) give

$$A_{s,t}^{ll'(\text{Coul,exch})} = -L^{-1} \int_0^R r dr \int_0^{2\pi} d\vartheta \int_0^R r' dr' \int_0^{2\pi} d\vartheta' F_{ll'}(r, r') D_{ll'}(\vartheta, \vartheta') \times$$

$$\times \left\{ \left[\cos^2 (c+a) \frac{L}{2} + \cos^2 (c-a) \frac{L}{2} \right] \frac{\pi}{c^2-a^2} \frac{1}{2} [c I_0(c\tilde{\omega}) - a I_0(a\tilde{\omega}) - \right.$$

$$- c\boldsymbol{L}_0(c\tilde{\omega}) + a\boldsymbol{L}_0(a\tilde{\omega})] -$$

$$-(\cos cL + \cos aL) \left[\frac{c^2}{c^2-a^2} \left\{ \frac{\cos cL}{c} \left[\frac{\pi}{2} - \text{Si}\,(cL) \right] I_0(c\tilde{\omega}) + M(c\tilde{\omega}) \right\} - \right.$$

$$\left. \left. - \frac{a^2}{c^2-a^2} \left\{ \frac{\cos aL}{a} \left[\frac{\pi}{2} - \text{Si}\,(aL) \right] I_0(a\tilde{\omega}) + M(a\tilde{\omega}) \right\} \right] \right\}. \tag{21}$$

Owing to (6), the integral $B_{s,t}^{ll'(\text{Coul,exch})}$ vanishes for $s \neq t$; hence,

$$I_{s,t}^{ll'(\text{Coul,exch})} = A_{s,t}^{ll'(\text{Coul,exch})}. \tag{22}$$

With the aid of Eqs (18)–(20) the integration in (21) can be completed. For even powers of $\tilde{\omega}$ the integration over r, r', ϑ and ϑ' is straightforward. In the case of odd powers, we can substitute

$$\tilde{\omega}^{2n+1} = \frac{\tilde{\omega}^{2n+2}}{\tilde{\omega}} = \tilde{\omega}^{2n+2} \sum_{m=0}^{\infty} P_m[\cos (\vartheta - \vartheta')] \left(\frac{r'}{r}\right)^m \tag{23}$$

for $r' < r$; P_m is the Legendre polynomial of order m. In Part I, Eq. (24), and in [2], Eq. (A 15), the odd powers of $\tilde{\omega}$ have been expressed in terms of the Gegenbauer coefficients C_m^ν. This was erroneous because C_m^ν are undefined quantities for $\nu = -1/2$.[1]

2.3. Integral for $s = t \neq 0$

In this case the integral is that of (3) with $c = a$. We have again

$$I_{t,t}^{ll'(\text{Coul,exch})} = A_{t,t}^{ll'(\text{Coul,exch})} + B_{t,t}^{ll'(\text{Coul,exch})} \tag{11a}$$

where

$$A_{t,t}^{ll'(\text{Coul,exch})} = -L^{-1} \int_0^R r dr \int_0^{2\pi} d\vartheta \int_0^R r' dr' \int_0^{2\pi} d\vartheta' F_{ll'}(r, r') D_{ll'}(\vartheta, \vartheta') \times$$

$$\times \int_0^\infty J_0(k\tilde{\omega}) (1 + \cos^2 aL - 2 \cos aL e^{-kL}) \frac{k^2}{(a^2 + k^2)^2} dk. \tag{24}$$

The integrand in (24) is that of $A_{s,t}^{ll'(\text{Coul, exch})}$ when $\lim_{c \to a}$ is calculated and Eq. (14) is taken into account. The second term inside the braces of (12) has been neglected because by virtue of Eq. (6) $\cos^2 aL - 1$ is zero.

The integral (24) can be calculated either directly, or as the $\lim_{c \to a}$ of the expression (21). In the first case the integration can be performed with the aid of Section 13.6 of [6]. The last term in the integrand of (24) can be transformed into $e^{-kL}(a^2 + k^2)^{-1} - a^2 e^{-kL}(a^2 + k^2)^{-2}$; then the integral of the first component is that of Eq. (17) and the integral of the second component can be obtained from the first one by differentation with respect to parameter a. We follow the second way, taking into account that the integrand in (12) is a continuous function of k, c and a for any real c and a except when $c = a = 0$ (the singularity in the last term of the integrand in (12) is spurious). We have

$$\lim_{c \to a} [cI_0(c\tilde{\omega}) - aI_0(a\tilde{\omega}) - c\boldsymbol{L}_0(c\tilde{\omega}) + a\boldsymbol{L}_0(a\tilde{\omega})] \frac{1}{c^2 - a^2} =$$

$$= \frac{1}{2a} \frac{d}{dx} [xI_0(x) - x\boldsymbol{L}_0(x)] \Big|_{x = \tilde{\omega}a}; \tag{25}$$

$$\lim_{c \to a} \frac{1}{c^2 - a^2} \left\{ c \cos cL \left[\text{Si}\,(cL) - \frac{\pi}{2} \right] I_0(c\tilde{\omega}) + c^2 M(c\tilde{\omega}) - \right.$$

$$\left. - a \cos aL \left[\text{Si}\,(aL) - \frac{\pi}{2} \right] I_0(a\tilde{\omega}) - a^2 M(a\tilde{\omega}) \right\} =$$

$$= \frac{1}{2a} I_0(a\tilde{\omega}) \frac{d}{dx} \left\{ x \cos xL \left[\text{Si}\,(xL) - \frac{\pi}{2} \right] \right\} \Big|_{x=a} +$$

[1] I am indebted to Dr P. J. Roberts for drawing my attention to this point.

$$+\frac{1}{2}\cos aL\left[\text{Si}\,(aL)-\frac{\pi}{2}\right]\frac{d}{dx}\left[I_0(\tilde{\omega}x)\right]\Big|_{x=a}+$$

$$+\frac{1}{2a}\frac{d}{dx}\left[x^2M(\tilde{\omega}x)\right]\Big|_{x=a}. \qquad (26)$$

Taking into account that

$$\frac{d}{dy}\left[yI_0(y)\right]=yI_1(y)+I_0(y) \qquad (27)$$

and

$$\frac{d}{dy}\left[y\boldsymbol{L}_0(y)\right]=y\boldsymbol{L}_1(y)+\left[\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{3}{2}\right)\right]^{-1}y+\boldsymbol{L}_0(y), \qquad (28)$$

where y is a variable, we obtain

$$A_{t,t}^{ll'(\text{Coul,exch})}=-L^{-1}\int_0^R rdr\int_0^{2\pi}d\vartheta\int_0^R r'dr'\int_0^{2\pi}d\vartheta' F_{ll'}(r,r')D_{ll'}(\vartheta,\vartheta')\times$$

$$\times\left\{(\cos^2 aL+1)\frac{\pi}{4a}\left[I_0(\tilde{\omega}a)+a\tilde{\omega}I_1(a\tilde{\omega})-\boldsymbol{L}_0(a\tilde{\omega})-a\tilde{\omega}\boldsymbol{L}_1(a\tilde{\omega})-a\tilde{\omega}\Gamma^{-1}\left(\frac{3}{2}\right)\Gamma^{-1}\left(\frac{1}{2}\right)\right]+\right.$$

$$+2\cos aL\left\{\frac{\cos aL}{2a}\left[\text{Si}\,(aL)-\frac{\pi}{2}\right]\left[I_0(a\tilde{\omega})+a\tilde{\omega}I_1(a\tilde{\omega})\right]-\right.$$

$$\left.\left.-M(a\tilde{\omega})-\frac{a}{2}\frac{dM(a\tilde{\omega})}{da}\right\}\right\}, \qquad (29)$$

where the terms which vanish owing to Eq. (6) have been omitted. The integration over r, r', ϑ and ϑ' can be completed when Eq. (23) is used.

The contribution of the $B_{t,t}$ terms does not vanish and its calculation seems to be easier without the aid of (14); we have

$$B_{t,t}^{ll'(\text{Coul,exch})}=\sum_{m=0}^{\infty}\varepsilon_m\int_0^{2\pi}d\vartheta\int_0^{2\pi}d\vartheta'\cos\left[m(\vartheta-\vartheta')\right]B_{t,t}^{ll'(m)(\text{Coul,exch})}\times$$

$$\times D_{ll'}(\vartheta,\vartheta'), \qquad (30)$$

where

$$B_{t,t}^{ll'(m)(\text{Coul,exch})}=\int_0^R rdr\int_0^R r'dr'F_{ll'}(r,r')\int_0^{\infty}J_m(kr)J_m(kr')\frac{kdk}{a^2+k^2}=$$

$$=\int_0^R rdr\int_0^R r'dr'F_{ll'}(r,r')I_m(ar)K_m(ar') \qquad (31)$$

which holds for $r' > r$; for $r' > r$ a reversed sequence of the arguments should occur [6];

$$K_m(z) = \frac{1}{2} \sum_{\nu=0}^{m-1} \frac{(-1)^\nu (m-\nu-1)!}{\nu!(\frac{1}{2} z)^{m-2\nu}} +$$

$$+(-1)^{m+1} \sum_{\nu=0}^{\infty} \frac{(\frac{1}{2})^{m+2\nu}}{\nu!(m+\nu)!} [\ln (\tfrac{1}{2} z) - \tfrac{1}{2} \psi(\nu+1) - \tfrac{1}{2} \psi(m+\nu+1)], \quad (32)$$

where $\psi(q)$ is $1+\frac{1}{2}+\frac{1}{3}+\ldots+\frac{1}{q}-\gamma$ (γ is Euler's constant), and I_m is given in Eq. (18) with ar (or ar') instead of $b\tilde{\omega}$. Equations (32) and (18) allow term-by-term integration in (31).

Owing to the equation

$$\int_0^{2\pi} d\vartheta \int_0^{2\pi} d\vartheta' \cos [m(\vartheta-\vartheta')] \cos n\vartheta \cos n'\vartheta' = 0, \quad (33)$$

which holds unless $m = n = n'$, the sum (30) may be reduced to only a few terms. We obtain

$$B_{t,t}^{00(\text{Coul,exch})} = B_{t,t}^{00(0)(\text{Coul,exch})} \quad (34a)$$

$$B_{t,t}^{11(\text{Coul,exch})} = B_{t,t}^{11(0)(\text{Coul,exch})} + \tfrac{1}{2} B_{t,t}^{11(2)(\text{Coul,exch})} \quad (34b)$$

for the $\sigma-\sigma$ and $\pi-\pi$ interactions, respectively, and

$$B_{t,t}^{01(\text{Coul})} = B_{t,t}^{01(0)(\text{Coul})} \quad (34c)$$

$$B_{t,t}^{01(\text{exch})} = B_{t,t}^{01(1)(\text{exch})} \quad (34d)$$

for the $\pi-\sigma$ interaction.

2.2. Integrals for $s = t = 0$

Here we do not obtain separate convergent results when the limits of (24) and (3) are calculated for $a \to 0$. For example,

$$A_{0,0}^{ll'(\text{Coul})} = \lim_{a\to 0} A_{t,t}^{ll'(\text{Coul})} = -2 \int_0^R rdr \int_0^{2\pi} d\vartheta \int_0^R r'dr' \int_0^{2\pi} d\vartheta' \times$$

$$\times F_{ll'}(r, r') D_{ll'}(\vartheta, \vartheta') L^{-1} \int_0^\infty k^{-2}[1-\exp(-Lk)] J_0(k\tilde{\omega}) dk \quad (35)$$

is a divergent term for any finite positive R. This is evident when the integral $\int_0^\infty dk$ in (35) is divided into

$$\int_0^g dk + \int_g^\infty dk, \quad (36)$$

where g is a finite positive number, and the term under the first integral sign is expanded into a series of powers of $k\tilde{\omega}$. There is a similar divergence in the case of $B_{0,0}^{ll'(\mathrm{Coul})}$. But the total interaction integral

$$I_{0,0}^{ll'(\mathrm{Coul})} = A_{0,0}^{ll'(\mathrm{Coul})} + B_{0,0}^{ll'(\mathrm{Coul})} =$$

$$= L^{-1}\int d\tau \int d\tau' \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} F_{ll'}(r, r')D_{ll'}(\vartheta, \vartheta') =$$

$$= L^{-1}\int_0^R rdr \int_0^{2\pi} d\vartheta \int_0^R r'dr' \int_0^{2\pi} d\vartheta' F_{ll'}(r, r')D_{ll'}(\vartheta, \vartheta') \int_0^\infty J_0(k\tilde{\omega})dk \times$$

$$\times 2\left[\frac{L}{k} + \frac{e^{-kL}-1}{k^2}\right] =$$

$$= L^{-1}\int_0^R rdr \int_0^{2\pi} d\vartheta \int_0^R r'dr' \int_0^{2\pi} d\vartheta' F_{ll'}(r, r')D_{ll'}(\vartheta, \vartheta') \times$$

$$\times 2L\left[\ln\left(\frac{L}{\tilde{\omega}} + \sqrt{\left(\frac{L}{\tilde{\omega}}\right)^2+1}\right) - \sqrt{1+\left(\frac{\tilde{\omega}}{L}\right)^2} + \frac{\tilde{\omega}}{L}\right] \qquad (37)$$

converges. The result (37) can be obtained if we notice that

$$\frac{L}{k} + \frac{e^{-kL}-1}{k^2} = \frac{1}{k}\int_0^L (1-e^{-xk})dx \qquad (38)$$

and [7]

$$\int_0^\infty \frac{1-e^{-xk}}{k} J_0(k\tilde{\omega})dk = \ln\left[\frac{x}{\tilde{\omega}} + \sqrt{\left(\frac{x}{\tilde{\omega}}\right)^2+1}\right]. \qquad (39)$$

Equation (37) can be obtained by integrating (39) over x from 0 to L. The integrand in (37) can again be expanded into a series [8] and the integration completed.

3. *Terms important at R tending to zero*

These terms are needed for a further discussion. In the case of $A_{s,t}^{ll'(\mathrm{Coul,\,exch})}$, also for $s = t$, only the terms with $\tilde{\omega}^0$ in the integrand give a non-vanishing contribution at $R \to 0$. We obtain

$$\lim_{R\to 0} A_{s,t}^{ll(\mathrm{Coul,exch})} = \lim_{R\to 0} A_{s,t}^{l'l'(\mathrm{Coul,exch})} = \lim_{R\to 0} A_{s,t}^{ll'(\mathrm{Coul})} \qquad (40)$$

and, for $l \neq l'$,

$$\lim_{R\to 0} A_{s,t}^{ll'(\mathrm{exch})} = 0, \qquad (41)$$

where the last equation is due to the orthogonality of $\cos l\vartheta$ and $\cos l'\vartheta$. Equation (40) and (41) are also valid for $s = t$. The exact value for (40) will be given in a forthcoming paper.

Because Eq. (22) holds, the further examination of integrals may be limited only to $B_{t,t}^{ll'(m)}$ in Eqs (34). In each case the non-vanishing term (nv) at $R \to 0$ is that which has

$$R^n, R^m \ln R \tag{42}$$

with the power exponent $n = m = 0$. Starting with $l = l' = 0$, with the aid of (32), we find

$$[B_{t,t}^{00(0)(\mathrm{Coul,exch})}]_{nv} = \int_0^R rdr\{\int_0^r r'dr'[-\ln(ar)+\ln 2-\gamma]+$$

$$+\int_r^R r'dr'[-\ln(ar')+\ln 2-\gamma]\}F_{00}(r,r') =$$

$$= -\ln a+\ln 2-\gamma+Z_{00}(R) \tag{43}$$

where

$$Z_{00}(R) = \int_0^R rdr(-\ln r\int_0^r r'dr' - \int_r^R r'\ln r'dr')F_{00}(r,r') =$$

$$= (Q_0)^4\left[\frac{R^4}{16}-\frac{R^4}{4}\ln R\right] + \text{terms in } u_0^2 \text{ and higher powers of } u_0. \tag{44}$$

The second term inside the square brackets in (44) gives the logarithmic divergence at $R \to 0$ and similar divergences give the terms named after the square brackets. The terms in (43) before Z_{00} are due to normalization. The same result occurs in $B_{t,t}^{11(0)(\mathrm{Coul,\,exch})}$ and $B_{t,t}^{01(0)(\mathrm{Coul})}$. Only Z terms change with l and, all being independent of a, have divergences analogous to that of (44).

On the other hand, again with the aid of (32),

$$[B_{t,t}^{11(2)(\mathrm{Coul,exch})}]_{nv} = \int_0^R rdr\left[\frac{2}{a^2r^2}\int_0^r r'\frac{1}{2!4}(ar')^2dr'+\right.$$

$$\left.+\frac{1}{2!4}(ar)^2\int_r^R\frac{2}{(ar')^2}r'dr'\right]F_{11}(r,r') \tag{45}$$

which gives $n = 0$; the lowest m of $B_{t,t}^{11(2)(\mathrm{Coul.\,exch})}$ is 4. In the case of (34d) the term with $n = 0$ is given by

$$[B_{t,t}^{01(1)(\mathrm{exch})}]_{nv} = \int_0^R rdr\left[\frac{1}{ar}\int_0^r r'(\tfrac{1}{2}ar')dr'+\right.$$

$$\left.+(\tfrac{1}{2}ar)\int_r^R r'\frac{1}{ar'}dr'\right]F_{01}(r,r'), \tag{46}$$

the term with the lowest m being that with $m = 2$. Finally, in the case of $I_{0,0}^{ll'(\mathrm{Coul})}$, the terms of (42) with $n = m = 0$ are given by the first terms in the series developments of $\sqrt{1+\left(\frac{\tilde{\omega}}{L}\right)^2}$ and

$$\ln\left[\frac{L}{\tilde{\omega}}+\sqrt{\left(\frac{L}{\tilde{\omega}}\right)^2+1}\right] \equiv \mathrm{sh}\left(\frac{L}{\tilde{\omega}}\right) =$$

$$= \ln(2L/\tilde{\omega}) + \sum_{n=1}^{\infty} (-1)^{n+1} \frac{(2n)!\left(\frac{L}{\tilde{\omega}}\right)^{-2n}}{2^{2n}(n!)^2 2n}. \quad (47)$$

The last expression is valid for $L^2 > \tilde{\omega}^2$ and, in particular, holds for very small R. The integration (37) for the constant terms of the developments is trivial, giving back those terms, so there remains the integral of $-\ln\tilde{\omega}$ in (47). We take as an example $l = l' = 0$ and retain only the first term $(= 1)$ in the development of the J_0-product. We obtain:

$$-4Q_0^4 T_0^4 \int_0^R r dr \int_0^R r' dr' \int_0^{2\pi} d\vartheta \int_0^{\pi} d\chi \ln\tilde{\omega} =$$

$$= -\frac{2}{\pi} Q_0^4 \int_0^R r dr \int_0^{\pi} d\chi \left\{ \int_0^r r' dr' \left[\ln r + \frac{1}{2}\ln(1+\alpha^2-2\alpha\cos\chi)\right] + \right.$$

$$\left. + \int_r^R r' dr' \left[\ln r' + \tfrac{1}{2}\ln(1+\alpha'^2-2\alpha'\cos\chi)\right] \right\} =$$

$$= -2Q_0^4 \{ \int_0^R r dr [\ln r \int_0^r r' dr' + \int_r^R r' \ln r' dr'] \} =$$

$$= -2Q_0^4 (\tfrac{1}{4} R^4 \ln R - \tfrac{1}{16} R^4). \quad (48)$$

In (48) we have replaced $\vartheta - \vartheta'$ by χ and the integration over ϑ and ϑ' by that over ϑ and χ. The terms involving $\ln(\cos\chi)$ vanish due to the integration over χ [7]; $\alpha = r'/r$ and $\alpha' = r/r'$. The integration of further terms in $F_{00}(r, r')$, as well as that with the Coulomb $F_{ll'} D_{ll'}$ other than for $l = l' = 0$, can be performed in a similar way. These integrals, as well as that of Eq. (48), give at $R \to 0$ divergences identical to that of Eq. (44).

4. Electron-nucleus interaction integrals

The essential part of these integrals has been calculated correctly in [9]. However, in order to make the presentation of the interaction problem as complete as possible, and also to remove a minor error, we give now the corresponding derivation in a more detailed form than before. In general, any FE electron-nucleus integral can be represented in terms of

$$H_{nm}^{ll'\mathrm{core}} = S_{n-m}^{ll'} - S_{n+m}^{ll'} \quad (49)$$

where

$$S_p^{ll'} = \frac{1}{L} N_l N_{l'} \int_0^L \cos czdz \int_0^R J_l(u_l r) J_{l'}(u_{l'} r) \int_0^{2\pi} \cos l\vartheta \cos l'\vartheta \frac{(-Ze^2)}{|\boldsymbol{r}-\boldsymbol{a}_j|} rdrd\vartheta. \tag{50}$$

Here, Ze is the nuclear charge, $N_l = Q_l T_l$, and the same holds for l'. Vector $\boldsymbol{a}_j$ is the position of the nucleus on the axis of the cylindrical potential box,

$$c = \frac{p\pi}{L} \tag{51}$$

where p is an integer. Instead of following the procedure of [9], we directly use $(|\boldsymbol{r}-\boldsymbol{a}_j|)^{-1}$ as given in (10). Since $a_{jr} = 0$ and $a_{jz} = |\boldsymbol{a}_j| = a_j$, we have

$$S_p^{ll'} = \frac{1}{L} N_l N_{l'}(-Ze^2) \int_0^L \cos cz \int_0^R J_l(u_l r) J_{l'}(u_{l'} r) \times$$

$$\times \int_0^{2\pi} \cos l\vartheta \cos l'\vartheta \int_0^\infty J_0(kr) e^{-k|z-a_j|} dkdzrdrd\vartheta, \tag{52}$$

because other terms in the development (10) vanish. We see that $S_p^{ll'} = 0$ unless $l = l'$. When the last case holds, the integration over ϑ gives 2π for $l = l' = 0$, and π otherwise. The sequence of the integrations over z and k can be interchanged because there is uniform convergence of the integral over k in the whole interval of z (see the inferences below Eq. (10)). Two cases can be distinguished: (*i*) when $p = 0$ and (*ii*) $p \neq 0$. In the first case

$$S_0^{ll} = \frac{1}{L}(-Ze^2) Q_l^2 \int_0^R J_l^2(u_l r) rdr \times$$

$$\times \int_0^\infty [2 - e^{-ka_j} - e^{-k(L-a_j)}] k^{-1} J_0(kr) dk, \tag{53}$$

which — due to [7] and Eq. (39) — becomes

$$S_0^{ll} = \frac{1}{L}(-Ze^2) Q_l^2 \int_0^R J_l^2(u_l r) rdr \times$$

$$\times \left\{ \ln\left[\frac{a_j}{r} + \sqrt{\left(\frac{a_j}{r}\right)^2 + 1}\right] + \ln\left[\frac{L-a_j}{r} + \sqrt{\frac{(L-a_j)^2}{r^2} + 1}\right]\right\}. \tag{54}$$

Following *e.g.* [8] (*cf.* also Eq. (47)) the contents of the braces can be represented as a sum of sh (hyperbolic sine).

On the other hand, for $p \neq 0$,

$$S_p^{ll} = \frac{1}{L}(-Ze^2)Q_l^2 \int_0^R J_l^2(u_l r) r dr \times$$

$$\times \int_0^\infty dk \left[2k \frac{\cos ca_j}{c^2+k^2} - \frac{ke^{-ak}}{c^2+k^2} - \cos cL \frac{ke^{-(L-a_j)k}}{c^2+k^2} + \right.$$

$$\left. + \frac{c \sin cL}{c^2+k^2} e^{-(L-a_j)k} \right]. \tag{55}$$

The last term in the square brackets vanishes because of Eq. (51). We obtain

$$S_p^{ll} = \frac{1}{L} Q_l^2(-Ze^2) \int_0^R J_l^2(u_l r) r dr \times$$

$$\times \left[2 \cos (ca_j) K_0(cr) - \left\{ \sin (ca_j) \left[\frac{\pi}{2} - \mathrm{Si}\,(ca_j) \right] - \cos (ca_j)\, \mathrm{Ci}\,(ca_j) \right\} I_0(cr) - \right.$$

$$- \cos cL \left\{ \sin [c(L-a_j)] \left[\frac{\pi}{2} - \mathrm{Si}\,(c(L-a_j)) \right] - \cos [c(L-a_j)]\, \mathrm{Ci}\,[c(L-a_j)] \right\} I_0(cr) -$$

$$\left. - P_{a_j}(cr) - \cos (cL) P_{L-a_j}(cr) \right] \tag{56}$$

which — with Eq. (51) taken into account — reduces to the formula (7) in [9] except here we have the terms $\cos cL$ erroneously omitted in [9]. Due to these terms and Eq. (51) we have no change of sign at Si and Ci, irrespectively of whether cL is an even or an odd multiple of π. Because cL/π can be only an even integer (see [9] and the forthcoming paper), the formula (7) in [9] could give correct results. In Eq. (56) we have

$$P_{a_j}(cr) = \sum_{m=1}^{m=\infty} (-1)^m \frac{(2m-1)!}{(ca_j)^{2m}} \sum_{n=m}^{n=\infty} \left(\frac{cr}{2} \right)^{2n} \frac{1}{(n!)^2}, \tag{57}$$

and the analogous formula is valid for P_{L-a_j}. Equation (57) is identical with the corresponding expression given in [9].

5. *Summary*

All the integrals due to the electron-electron operator in the three-dimensional FE model (Coulomb, exchange and those for the configurational interaction with $l = l'$ inside any configuration) can be composed from the formulae given in Section 2. For the case of $s = t$ not only terms A but also terms B are important. The three-dimensional FE integrals for the electron-core interaction can be established in terms of the expressions given in Section 4.

The case when the radius of the potential box tends to zero is of special interest for further investigations and the corresponding formulae for the electron-electron operator have been set off in Section 3. They cancel the erroneous statement of Part I that at $R \to 0$ all electron-electron integrals converge and for the $\pi - \pi$ interaction are larger than those for the $\sigma - \sigma$ interaction by a factor of 3/2. The electron-core interaction at $R \to 0$ can be examined in terms of Eq. (54), with the equation corresponding to (47), and Eq. (56) with the series development for K_0 and P.

A detailed examination of the effects at $R \to 0$ will be the subject of a forthcoming converge and paper.

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