

INTERACTION OF SIGMA AND PI ELECTRONS IN THE FREE-ELECTRON MODEL. III. RIGOROUS APPROACH TO THE ONE-DIMENSIONAL MODEL

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A rigorous approach to the electron-electron and electron-core interaction has been performed for the case of the radius of the free-electron potential box tending to zero. Also an alternative approach, in which the free-electron model is from the beginning of one-dimensional character, has been developed. With a certain supplementary assumption made in the second scheme, a full parallelism concerning the convergence-divergence problem exists between the both approaches. Contrary to a previous non-rigorous treatment of the electron-electron interaction by the author, all interaction integrals — except the pi-sigma exchange integral — diverge in the present theory. But the differences of the interaction terms which contribute to the energies of the electron excitations converge in many cases. The electron-core matrix elements converge only when the Ruedenberg-Scherr conditions for the free-electron model are fulfilled.

1. Electron-electron interaction $R \rightarrow 0$

In a preceding paper [1] we recalculated the interaction integrals for a three-dimensional free-electron model. Now the integrals undergo a limiting procedure of $R \rightarrow 0$. This gives, for the electron-electron interaction,

$$\begin{aligned} \lim_{R \rightarrow 0} A_{s,t}^{(Coul, \text{exch})} &= -L^{-1} \left[\frac{\pi}{c+a} \cos^2 \left(\frac{c+a}{2} L \right) + \right. \\ &+ \left. (\cos cL + \cos aL) \frac{c \operatorname{si}(cL) \cos cL - a \operatorname{si}(aL) \cos aL}{c^2 - a^2} \right] = \\ &= -\pi^{-1} \{ [1/(s+t)] [\operatorname{Si}(s\pi) + \operatorname{Si}(t\pi)] + [1/(s-t)] [\operatorname{Si}(s\pi) - \operatorname{Si}(t\pi)] \} \end{aligned} \quad (1)$$

where $\operatorname{si}(x) = \operatorname{Si}(x) - \pi/2$. The second equation in (1) is due to Eq. (6) of [1]. It holds unless s and t are of different parity. When this last case occurs, expression (1) is zero.

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The same happens when one subscript is zero and another is an odd integer. Expressions (1) — with the accuracy to a constant multiplier — are equal to those of [2] and [3].

At the second step, we have (cf. [1])

$$\begin{aligned} \lim_{R \rightarrow 0} A_{t,t}^{ll'(\text{Coul, exch})} &= -L^{-1} \left\{ \frac{\pi}{2a} \cos^2 aL + \frac{\cos^2 aL}{a} \left[\text{Si}(aL) - \frac{\pi}{2} \right] \right\} = \\ &= -(t\pi)^{-1} \text{Si}(t\pi), \end{aligned} \quad (2)$$

where Eq. (6) of [1] again has been taken into account. Eq. (2) also is the $\lim_{c \rightarrow a}$ of expression (1). The behaviour of Eqs (1) and (2) with respect to l and l' is referred to in [1], Section 3 and Section 5.

On the other hand,

$$\lim_{R \rightarrow 0} B_{s,t}^{ll'(\text{Coul, exch})} = 0 \quad (3)$$

for $s \neq t$, because the term $B_{s,t}^{ll'(\text{Coul, exch})}$ vanishes identically for any finite R owing to the FE boundary conditions; the components of (3) are:

$$\lim_{R \rightarrow 0} (0 \ln R) = 0 \quad (4)$$

and zero times a constant. But in the case of $s = t$, Eq. (3) does not apply. The terms $\lim_{R \rightarrow 0} B_{t,t}^{ll'(\text{Coul, exch})}$ diverge, as it has been noted already in [1] and the Appendix of [3]. The exception is the exchange term with $l \neq l'$. For example, when $l = 0$ and $l' = 1$, or *vice versa*, we obtain — with the aid of Eqs (2), (34d), (41) and (46) of [1] — a convergent result for any B -term at $R \rightarrow 0$ and the corresponding π - σ exchange integral equals $0.58 (e^2/L)$. The function $J_0(u_0r)$ entering F_{01} in (46) of [1] has been approximated inside the interval $0 \leq r \leq R$ by $\cos(\pi r/2R)$ and $J_1(u_1r)$ by a function proportional to $\sin(\pi r/R)$; the same has been done for variable r' and the normalization coefficients have been changed accordingly. A characteristic point is that $\lim_{R \rightarrow 0} B_{t,t}^{01(\text{exch})}$ does not depend on t .

Also — in virtue of Section 2.3 and 3 of [1] — converges the difference

$$\begin{aligned} \lim_{R \rightarrow 0} [B_{t,t}^{ll'(\text{Coul, exch})} - B_{s,s}^{ll'(\text{Coul, exch})}] &= \\ &= -\ln a + \ln c = -\ln t + \ln s. \end{aligned} \quad (5)$$

The result holds with the exception of the exchange case with $l \neq l'$ when expression (5) is zero.

2. Electron-nucleus interaction at $R \rightarrow 0$

With the series development of Eq. (54) in [1] and the normalization of $J_l(u_r)$, we obtain

$$\begin{aligned} \lim_{R \rightarrow 0} S_0^{ll} &\equiv \lim_{R \rightarrow 0} S_0^{ll(a_j)} = \\ &= (-Ze^2/L) [\ln a_j + \ln(L - a_j) + 2 \ln 2 + \lim_{R \rightarrow 0} Y(u_l; R)] \end{aligned} \quad (6)$$

where $\lim_{R \rightarrow 0} Y(u_i; R)$ contains a divergent component

$$\lim_{R \rightarrow 0} \ln R; \quad (7)$$

in a similar manner diverges (*cf.* also [4])

$$\begin{aligned} \lim_{R \rightarrow 0} S_p^{II} &\equiv \lim_{R \rightarrow 0} S_p^{II(a_j)} = \\ &= (-Ze^2/L) \left\{ 2 \cos(ca_j) (-\ln c + \ln 2 - \gamma) - \right. \\ &\quad \left. - \sin(ca_j) \left[\frac{\pi}{2} - \text{Si}(ca_j) \right] + \cos(ca_j) \text{Ci}(ca_j) - \right. \\ &\quad \left. - \cos cL \left\{ \sin[c(L-a_j)] \left[\frac{\pi}{2} - \text{Si}[c(L-a_j)] \right] - \cos[c(L-a_j)] \text{Ci}[c(L-a_j)] \right\} \right\} + \\ &\quad + (-Ze^2/L) \left[-\lim_{R \rightarrow 0} 2 \cos(ca_j) W(u_i; R) \right], \quad (8) \end{aligned}$$

where $c = p\pi/L$, because the last term in (8) contains again a divergent component of (7). $W(u_i; R)$ follows from the development of K_0 in Eq. (56) of [1]. It represents the integral

$$Q_i^2 \int_0^R r \ln r J_i^2(u_i r) dr \quad (9)$$

which has the lowest power of R . For example, for $l = 0$,

$$\begin{aligned} W(u_0; R) &= Q_0^2 \left(\frac{1}{2} R^2 \ln R - \frac{1}{4} R^2 \right) + \\ &+ \text{terms with } u_0^2 \text{ and higher powers of } u_0. \quad (10) \end{aligned}$$

The dependence on R of terms named in the second row of (10) is similar to that of the first row. Let us note that $W(u_i; R)$ does not depend on c .

3. Application to the electron excitation energies

3.1. Contribution due to the electron-electron interaction

Due to the behaviour of the $B_{i,l}$ terms and that of $I_{0,0}^{II}$ (see [1]), all Coulomb and exchange integrals for π and σ orbitals — except the exchange integral for the $\pi-\sigma$ interaction — diverge at $R \rightarrow 0$. But, in many cases, we are interested rather in energy differences than energies themselves. Then the one-dimensional FE model may be of use. For example the difference

$$\lim_{R \rightarrow 0} (J_{nm}^{II'} - J_{n'm'}^{II'}) \quad (11)$$

is convergent in most cases. We can interpret (11) as the difference in the Coulomb energy of an electron pair which occupy first the one-electron levels n and m and then the levels n' and m' . Expression (11) diverges only when $n = m$ or $n' = m'$. When both equalities hold, Eq. (11) is still convergent due to Eqs (2) and (5). A similar convergence exists for the difference between two exchange integrals

$$\lim_{R \rightarrow 0} (K_{nm}^{II'} - K_{n'm'}^{II'}), \quad (12)$$

though the physical meaning of the difference is less evident. Eq. (12) is convergent for any n, m, n' and m' , remembering that for the exchange terms we have $n \neq m$ and $n' \neq m'$. Explicit expressions for (11) and (12) are given in a subsequent paper (Part IV, Eqs (4)–(8)).

Let us now examine the contribution of the first-order electron interaction effects to an one-electron excitation energy. Following *e. g.* [5], the energy difference between the centre of gravity of excited singlet and triplet and the closed-shell (singlet) ground state is

$$\Delta E^{ee(1)} = \sum_i (2J_{n_2 i}^{II'} - K_{n_2 i}^{II'}) - \sum_i (2J_{n_1 i} - K_{n_1 i}) - J_{n_2 n_1} + K_{n_2 n_1}. \quad (13)$$

The index n_2 denotes an excited one-electron level, the index n_1 — a ground-state level left in the excitation; the summation runs over all levels of the closed-shell ground state. We assume that only the z -component of the FE wavefunction changes during the excitation *i. e.* n_1 and n_2 are different values for n in Eq. (1) of [6] (Part I). Due to Section 1, expression (13) diverges at $R \rightarrow 0$. However, convergent results can be obtained for the two-electron excitation energies of a system, provided that the character of the electron distribution among the one-electron levels — an open-shell or a closed-shell — does not change during the excitation. For example, the excitation energy of two electrons promoted from level n_1 to level n_2 is a convergent difference

$$\Delta E^{ee(2)} = 2[\sum_i' (2J_{n_2 i} - K_{n_2 i}) - \sum_i' (2J_{n_1 i} - K_{n_1 i})] + J_{n_2 n_2} - J_{n_1 n_1} \quad (14)$$

provided that L is not changed in the excitation. The symbol Σ' denotes the sum with the omitted $i = n_1$.

We try to circumvent the difficulty due to the divergence of (13) by putting

$$\Delta E^{ee(1)} = \frac{1}{2} \Delta E^{ee(2)}. \quad (15)$$

The numerical results for (15) will be given in a subsequent paper. Let us note that the ratio of the number of terms changed by insertion of (15) into (13) to the total number of terms in (13), is a small quantity provided that large L (many electrons in a molecule) are considered.

An important drawback of the rigorous integrals for the electron-electron operator at $R \rightarrow 0$ is the divergence of many of the matrix elements entering the configurational inter-

¹ We remember that the level with n , or m , equal to zero does not exist in the FE model.

action when $l = l'$ inside a configuration. For example, among the elements calculated with the oversimplified scheme for butadiene [2], only one

$$[22|24] = (e^2/L) \lim_{R \rightarrow 0} (I_{4',6}^{ll'} - I_{0,6}^{ll'} - I_{2,4}^{ll'} + I_{0,2}^{ll'}) \quad (16)$$

is convergent in the rigorous theory; l and l' refer to electrons in different configurations. The examination of the matrix elements with $l \neq l'$ inside a configuration lies beyond the scope of the present.

3.2. Contribution due to the electron-core interaction

The electron-core contribution to the excitation energy between the levels n_2 and n_1 is

$$\lim_{R \rightarrow 0} \sum_j [H_{n_2 n_2}^{\text{core}(a_j)} - H_{n_1 n_1}^{\text{core}(a_j)}] = - \lim_{R \rightarrow 0} \sum_j [S_{p''}^{ll(a_j)} - S_{p'}^{ll(a_j)}] \quad (17)$$

where the summation runs over q point charges (nuclei) of the molecular core. Eq. (17) can converge when the coefficient by $W(u_j; R)$:

$$\sum_{j=1}^{j=q} (\cos p' a_j - \cos p'' a_j) = \sum_{j=1}^{j=q} \left(\cos \frac{2\pi n_1}{L} a_j - \cos \frac{2\pi n_2}{L} a_j \right) \quad (18)$$

vanishes (*cf.* Eq. (4)). In a similar way converges the nondiagonal electron-core matrix element

$$\lim_{R \rightarrow 0} \sum_j H_{mn}^{\text{core}(a_j)} = - \lim_{R \rightarrow 0} \sum_j [S_{m-n}^{ll(a_j)} - S_{m+n}^{ll(a_j)}] \quad (19)$$

provided that

$$\sum_{j=1}^{j=q} (\cos c' a_j - \cos c'' a_j) = \sum_{j=1}^{j=q} \left[\cos \left(\frac{m-n}{L} \pi a_j \right) - \cos \left(\frac{m+n}{L} \pi a_j \right) \right] \quad (20)$$

is zero. Eqs (18) and (20), when put equal to zero, can be transformed respectively into

$$\sum_{j=1}^{j=q} \sin^2 \left(\frac{\pi n_2}{L} a_j \right) = \sum_{j=1}^{j=q} \sin^2 \left(\frac{\pi n_1}{L} a_j \right) \quad (21)$$

and

$$\sum_{j=1}^{j=q} \sin \left(\frac{\pi m}{L} a_j \right) \sin \left(\frac{\pi n}{L} a_j \right) = 0. \quad (22)$$

These relations are the normalization and the orthogonality condition for the Ruedenberg-Scherr (RS) eigenvectors calculated in the case of a linear one-dimensional FE system [7]; in that case the coordinate a_j of the j th nucleus is equal to jd and L is $(q+1)d$ where d

is the CC length. Therefore, the fundamental properties of the RS eigenvectors, constructed from the values of the FE wave functions in the atomic positions, enable us to obtain the convergence of most of the electron-core excitation energies and non-diagonal matrix elements. Because these properties hold not only for linear but also branched systems, we can expect the convergence of $\sum_j [H_{n_2 n_2}^{\text{core}(a_j)} - H_{n_1 n_1}^{\text{core}(a_j)}]$ and $\sum_j H_{mn}^{\text{core}(a_j)}$ also in the case when: (i) the indices n_1, n_2, m and n denote the branched FE eigenstates, (ii) the summation runs over all sites of the branched core; and (iii) the RS boundary conditions for the branched FE path are fulfilled.

4. An alternative approach to the one-dimensional FE model

The integrals of preceding sections are obtained from the calculation made first in three dimensions and next when the radius R tends to zero. But the problem also can be viewed from the beginning in one dimension. This means we assume that the interaction between particles acts only in one direction, say that of variable z . In this case the interaction operator between an electron with coordinate at z and a nucleus which coordinate in z -direction is a_j is

$$(-Ze^2) \frac{1}{|z - a_j|}, \quad (23)$$

whereas that between an electron at z and another at z' is

$$\frac{e^2}{|z - z'|}. \quad (24)$$

Then in place of $\lim_{c \rightarrow a} I_{c,a}''$ (cf. Eq. (3) of [1]) we have [8]

$$\begin{aligned} \tilde{I}_{c,a}^{(R=0)} &= L^{-1} \int_0^L dz \int_0^L dz' \frac{1}{|z - z'|} \cos cz \cos az' = \\ &= L^{-1} \left\{ - \frac{\cos^2 \left[(c+a) \frac{L}{2} \right]}{c+a} [\text{Si}(cL) + \text{Si}(aL)] - \frac{\cos^2 \left[(c-a) \frac{L}{2} \right]}{c-a} [\text{Si}(cL) - \right. \\ &\quad \left. - \text{Si}(aL)] + \frac{1}{2} \left[\frac{\sin(c+a)L}{c+a} + \frac{\sin(c-a)L}{c-a} \right] \times \right. \\ &\quad \left. \times [-\ln c - \ln a + \text{Ci}(cL) + \text{Ci}(aL) - 2 \ln(0) - 2\gamma] \right\}, \quad (25) \end{aligned}$$

whereas in place of $\lim_{R \rightarrow 0} S_p^{II(a_j)}$ we have

$$\begin{aligned} \tilde{S}_p^{(a_j, R=0)} &= (-Ze^2/L) \int_0^L \frac{1}{|z-a_j|} \cos cz dz = \\ &= (-Ze^2/L) [-2 \cos(ca_j) \text{Ci}(0) + \\ &+ \cos(ca_j) \{\text{Ci}(ca_j) + \text{Ci}[c(L-a_j)]\} + \\ &+ \sin(ca_j) \{\text{Si}(ca_j) - \text{Si}[c(L-a_j)]\}]. \end{aligned} \quad (26)$$

Expression (25) has the undefined terms

$$0 \cdot \infty \quad (27)$$

where zero is due to Eqs (6) of [1], whereas for $c = a$ the integral (25) diverges. Also diverges the integral (26). But when we calculate: (i) the difference

$$\tilde{I}_{c,c}^{(R=0)} - \tilde{I}_{a,a}^{(R=0)}, \quad (28)$$

and (ii) the sum over the point charges of the core (with RS conditions for the core and the FE boundary) of a difference

$$\tilde{S}_p^{(a_j; R=0)} - \tilde{S}_w^{(a_j; R=0)}, \quad (29)$$

we obtain instead of divergences the terms (27), in each case identical to those entering Eq. (25). If we put a constant for any product (27), expressions (25), (28) and the sum of (29) converge, in analogy to (1)–(3) and (5) on the one hand, and (17) and (19) on the other. Let us note that apart from $(-Ze^2/L)$, the expression (29) is identical to that of Eq. (31) of Roberts [9].

A difficulty in the model given above is that it does not distinguish between $\pi-\pi$, $\sigma-\sigma$ and $\pi-\sigma$ interactions. This can be circumvented by considering the interaction of (23) and (24) averaged over the transversal components of the three-dimensional FE orbitals. Then the integral (23) is multiplied by $F_{ll'} D_{ll'}$ of [1] and integrated over r, r', ϑ and ϑ' . In effect, for Coulomb terms with any l and l' expression (23) is multiplied by 1, whereas the factor for the exchange terms is Kronecker's $\delta_{ll'}$. This provides again the term (27) for the $\pi-\sigma$ exchange integral, in correspondence with its convergence in the model of Section 1.

5. Summary

In a rigorous approach to the one-dimensional FE model all electron-electron interaction integrals — except the $\pi-\sigma$ exchange integral — diverge. The divergence of the Coulomb integrals can be assigned generally to

$$\lim_{R \rightarrow 0} I_{0,0}^{II}. \quad (30)$$

Eq. (30) gives the classic self-energy of the electron charge, so the identification of this energy with a convergent result, as it was done in the case of Part I and [10], is invalid.

The divergence of the Coulomb terms has been stressed recently in [9]. Contrary to the view expressed there, the divergence — though erroneously unnotified in Part I and [10] — is referred to by the present author in [3] (*cf.* the inferences below Eq. (A19) and Eq. (6)).

A similar situation exists for

$$\lim_{R \rightarrow 0} I_{s,s}^{ll'} \quad (31)$$

which — owing to the divergence of $\lim_{R \rightarrow 0} B_{s,s}^{ll'(\text{Coul})}$ and the same property of the exchange term for $l = l'$ — is divergent also for $s \neq 0$. This point seems to be overseen, and the corresponding integral incorrectly referred to, in [9]. Due to the divergence of (31), the exchange integrals as well as many of the matrix elements of the electron-electron configurational interaction diverge at $R \rightarrow 0$. But the two-electron excitation energies can converge and then used in an approximation to one-electron excitation energies; see Section 3.1.

The integrals for the electron-core interaction also diverge for $R \rightarrow 0$. Contrary to the view expressed in [9], the divergence is again referred to by the present author; see [4], p. 109. But, when a core is composed of point charges distributed equidistantly along the FE path with the condition at the boundary of [7], the electron-core excitation energies can converge (Section 3.2); also converge the majority of the matrix elements of the electron-core configurational interaction.

An approach to the electron-electron and electron-core interactions, in which the FE model is from the beginning one-dimensional and which is alternative to that outlined above, can be also developed. A full parallelism concerning the divergence-convergence problem exists between the both approaches provided that we put a constant for any of the expressions (27) in the second scheme. That is when the integrals and excitation energies are convergent in one approach, the analogous integrals and energies converge also in the second; a similar correspondence also holds for the case of the divergent terms.

The approach which is first three-dimensional and then assumes the radius $R \rightarrow 0$ seems to be physically more plausible; also different kinds of the interaction ($\pi-\pi$, $\pi-\sigma$ and $\sigma-\sigma$) can be easier distinguished in that scheme.

APPENDIX

Non-rigorous approach to the electron-electron interaction at $R \rightarrow 0$

This scheme has been applied in all numerical calculations on the electron interaction ($\pi-\pi$ and $\sigma-\sigma$) made previously by the author. Basing on rigorous integrals, the scheme can be postulated in the following way.

All integrals $J^{ll'}$ and $K^{ll'}$ can be expressed in terms of $I_{c,a}^{ll'}$ (see [1]). Hereafter we shall omit the indices ll' because for $R \rightarrow 0$ the terms $I_{c,a}^{ll'}$ are of equal value for any l (*cf.* [1], Section 3 and Section 1 of the present paper). Let us consider

$$i(c, a) = \lim_{R \rightarrow 0} I_{c,a} = \lim_{R \rightarrow 0} (A_{c,a} + B_{c,a}) \quad (32)$$

as a function of quantum parameters c and a ; we put

$$\alpha(c, a) = \lim_{R \rightarrow 0} A_{c,a} \quad (33)$$

and

$$\beta(c, a) = \lim_{R \rightarrow 0} B_{c,a}. \quad (34)$$

The properties of (32)–(34) are summarized on Fig. 1. First, we observe that (32) converges only in the points where c and a are integer multiples of π/L and $c \neq a$. These points are indicated by the circles; in points indicated by the full circles (s and t in Eq. (6) of [1] are of equal parity) $i(c, a)$ has the value given in Eq. (2), whereas on the open circles (s and t are of different parity) $i(c, a)$ is zero. In all other points of the (c, a) -space expres-

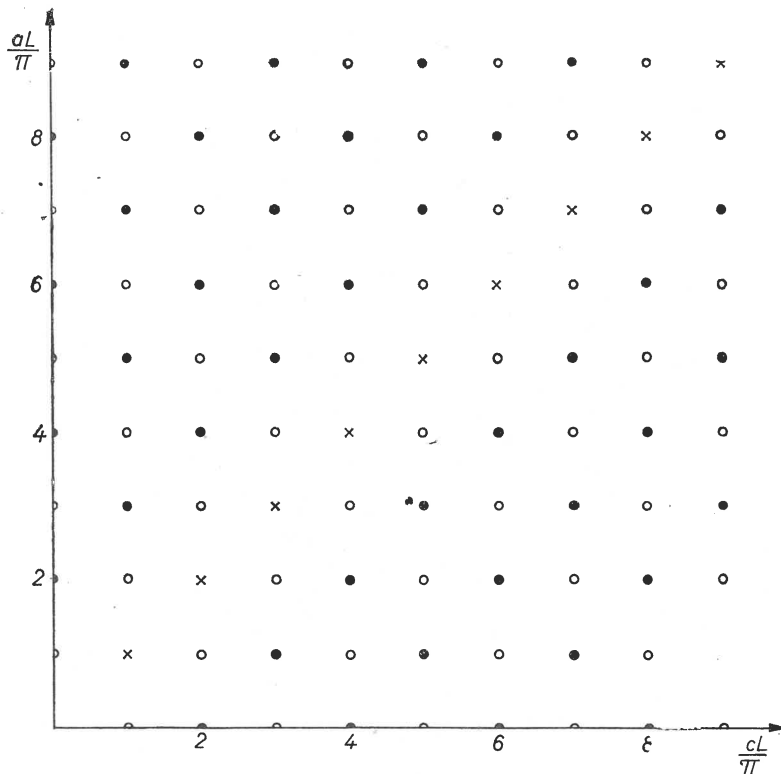


Fig. 1. Points of convergence of $i(c, a)$ (Eq. (32))

sion (32) diverges. More intrinsically, on all circles and crosses we have convergent $\alpha(c, a)$ and $\alpha(a, a)$, with the exception of $\alpha(0,0)$, whereas β converge on all circles, giving zero, but diverge on all crosses. Unfortunately, the points on the diagonal are important, because they enter twice to any exchange and at least once (the point $(0,0)$) to any Coulomb integral, causing the difficulties discussed in Section 3.

But the situation on crosses can be viewed also in another way, *viz.* we can consider the space composed only of points marked on Fig. 1 and corresponding to Eq. (6) of [1]. The space can be denoted by (\tilde{c}, \tilde{a}) and it is enough to take into account only a part of it, with $\tilde{c} > 0$ and $\tilde{a} > 0$. The space has its analogy in the solid state where it corresponds to that of the lattice sites; see *e. g.* [11]. In such a space β exhibits the behaviour similar to that of the Dirac δ function: it is everywhere zero except for the diagonal where it is infinite. But a choice of another value of β on the diagonal also seems to be possible. Instead of taking the rigorous β , let us consider it as a function of \tilde{c} and \tilde{a} according to the usual mathematical definition of a function. Then the limit of $\beta(\tilde{c}, \tilde{a})$ for $\tilde{c} \rightarrow \tilde{a}$ gives zero because the non-diagonal β represent a sequence of zeros. In effect, the divergent $i(\tilde{a}, \tilde{a})$, when substituted by the limit of $i(\tilde{c}, \tilde{a})$ for $\tilde{c} \rightarrow \tilde{a}$, give the convergent $i(\tilde{a}, \tilde{a})$ equal to $\alpha(\tilde{a}, \tilde{a})$.

The treatment as above is unjustified except that it works. In fact, it enables us to estimate rather accurately many of the physical data affected by the electron interaction in the linear unsaturated systems [2]–[4], [12]; for example, correct good values for the singlet-triplet separations have been obtained. From the point of view of the rigorous scheme this accuracy should be considered as accidental.

Let us note that the sign of α chosen in [2]–[4] and [6] is that which makes the exchange integrals positive. Contrary to the remark made at the end of the Appendix in [3] and in footnote 2 of [4], this sign is definable by the calculations; it is given correctly in Eq. (1). The sign given for S in [4] is that calculated for that integral.

An error in the π – π calculations was made still within the non-rigorous treatment. For, the shrinkage of the transversal box dimensions to zero gives equal $\alpha(\tilde{c}, \tilde{a})$ and $\alpha(\tilde{a}, \tilde{a})$ for different l ; see Section 3 and Section 5 of [1]. In effect, the factor of 3/2, which is introduced when the σ – σ interaction is replaced by that of π – π , should be unity.

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