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On the calculation of the interaction energy of defects in metals

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Abstract. — It is shown that the interaction energy of two defects in a metal can be computed consistently from one-electron effective potentials obtained by flattening out the Friedel oscillations of the electron charge density beyond a definite distance from each defect.

1. Introduction.

The Friedel theory of the screening of point defects in a metal [1] constitutes for metallic alloys an achievement comparable to that accomplished by Sommerfeld [2] for pure metals with the free electron gas obeying Fermi-Dirac statistics. In both cases quantum effects are essential.

The celebrated Friedel sum-rule :

\[ Z = \frac{2}{\pi} \sum_{\ell} (2 \ell + 1) \eta_{\ell}(\varepsilon_F) \]

relates the screening charge \( Z \) to the phase shifts \( \eta_{\ell} \) produced by the defect potential in the spherical partial waves of orbital momentum \( \ell \) at the Fermi level \( \varepsilon_F \) of the conduction electrons of the metal, when represented by a free electron gas. This rule shows clearly how the electronic screening charge of an impurity atom B dissolved in an otherwise pure metal A builds up in order to restore locally more or less of its neutral atom character to the B element. This charge extends roughly to the atomic sphere of B but, simultaneously, the phase shifts produced in the different spherical components of the wave-functions result in an oscillating variation of the electron density \( \rho(r) \) in the metal A, with an asymptotic behaviour at large distance \( r \) from B :

\[ \rho(r) \sim \text{const} \frac{\cos(2 k_F r + \eta)}{r^3} \]

where \( k_F \) is the Fermi radius of the electron gas and \( \eta \) some average phase shift. This is basically a quantum effect related to the discontinuity of occupation of the electron states at
the Fermi level. It is then obvious that these Friedel oscillations of the electronic charge density must give rise to long range interactions between defects in a metal [3]. In the case of magnetic impurities, they lead to spin glasses [4].

For going from the free electron Sommerfeld theory to a quantitative treatment of real pure metals, it was necessary to introduce the crystalline periodic potential into the band structure calculations and to take the Coulomb electron-electron interactions into account. Efficient numerical techniques have been devised for that and are extensively used with modern computing facilities. Some of the methods used in self-consistent band structure calculations can be rather naturally extended to the electronic structure of defects or impurities in dilute alloys or metallic compounds; they integrate then the energy spectrum of the Bloch states of the electron valence bands which are scattered by the defect. This is the case, for instance, for the Green function method [5] or the method of linearized «muffin-tin» orbitals in the atomic sphere approximation (LMTO-ASA) [6]. Numerous applications of these methods have been made during the last decade, generally in good quantitative agreement with experimental data.

At first sight, a major difficulty arises when one wishes to perform a self-consistent calculation of the interaction energy of two defects in a metal. Each of them creates long-range electron charge density oscillations, so that, strictly speaking, no atom is neutral any more. The charges of a given sign integrated in a spherical shell of radius \( r \) decrease only as \( r^{-1} \) and the successive shells interfere very far from each scattering center. This makes it illusory to attempt a fully self-consistent calculation. This state of affairs is corroborated by the following remark made by Stefanou while computing the charge and spin densities around a vanadium impurity dissolved in nickel-metal [7]. By increasing progressively the number of atomic shells included in a cluster treated self-consistently around the vanadium atom, he found that the electronic density stabilized itself rather rapidly inside the cluster while the oscillating charge density outside changed completely at each step.

Nevertheless, it seems possible to compute significant values for the interaction energy of defects even if the precise charge density at large distances cannot be calculated. Most of the present calculations of the electronic structure of metallic materials are based on the variational principle of Hohenberg and Kohn according to the Kohn and Sham formulation [8]. Exchange and electron correlation effects are usually taken into account in the local density approximation through the Hedin-Lundqvist interpolation formula [9]. According to the variational principle, given the electrostatic potential \( \nu \) of the nuclei, the ground state total energy of the electron-nuclei system is equal to the minimum value of some functional \( E_v[\rho] \) of the electronic density \( \rho (r) \), this value being obtained for the true self-consistent electronic density. A slightly different density \( \rho' \), if close enough to \( \rho \), will not change the total energy to first order and so can be used in a numerical calculation. This property has often been used in more or less equivalent forms for different applications, for instance the total energy and compressibility of homogeneous crystals [10]; it underlies the Natta and Toulouse proof [11] made on an approximate tight-binding model that the interaction energy of two point defects in a metal must decrease according to the \( r^{-3} \) law at large distances; this work was exploited later on in tight-binding models of dilute alloys involving transition metal impurities [12].

The purpose of the present article is to derive a precise prescription for the ab-initio calculation of the interaction energy of two defects in a metal. For simplicity, the derivation will be formulated for the case of two «point defects» although the method is quite general and could be extended in an obvious way to many other cases such as, for instance, the interaction energy between an impurity atom and a surface. Exchange and correlation effects will be considered only in the local density approximation.
2. Total energy with an approximate electron density.

Following Kohn and Sham theory, the ground state total energy of a system of electrons with density \( \rho (r) \) in the electrostatic potential \( v(r) \) of fixed nuclei is the minimum value of the density functional:

\[
E_v[\rho] = T[\rho] + \int \rho(r) v(r) \, d^3r + \frac{1}{2} \int \frac{\rho(r) \rho(r')}{|r-r'|} \, dr \, d^3r' + E_{xc}[\rho]
\]

where \( T[\rho] \) is the kinetic energy of a non-interacting electron gas with the same density \( \rho (r) \) in an appropriate effective potential \( v_{\text{eff}}(r) \) which has to be found self-consistently, and \( E_{xc}[\rho] \) defines the exchange and correlation energy. In the local density approximation, one takes:

\[
E_{xc}[\rho] = \int \rho(r) \, \varepsilon_{xc}(\rho) \, d^3r,
\]

\( \varepsilon_{xc}(\rho) \) being the exchange and correlation energy of a homogeneous electron gas with constant density \( \rho \). For an infinitesimal variation \( \delta \rho \) of the electron charge density such as to keep the total number of electrons constant, one gets:

\[
\delta E_v = \delta T + \int \delta \rho \, v \, d^3r + \int \frac{\delta \rho(r) \rho(r')}{|r-r'|} \, dr \, d^3r' + \int \delta \rho \, v_{xc}(\rho) \, d^3r
\]

where:

\[
v_{xc}(\rho) = \frac{\partial}{\partial \rho} [\rho \varepsilon_{xc}(\rho)]
\]

defines the « exchange and correlation potential ». For the same variation \( \delta \rho \), the change in energy of the associated non-interacting electron system is:

\[
\delta E_s = \delta T + \int \delta \rho \, v_{\text{eff}}(r) \, d^3r.
\]

The condition of minimum:

\[
\frac{\delta E_v}{\delta \rho} = \frac{\delta E_s}{\delta \rho} = 0,
\]

determines the effective potential:

\[
v_{\text{eff}}(r) = v(r) + \int \frac{\rho(r')}{|r-r'|} \, d^3r' + v_{xc}(\rho).
\]

This potential must be computed self-consistently through an iterative procedure from the one-electron Schrödinger equation:

\[
-\frac{\Delta}{2} \psi + V_{\text{eff}} \psi = \varepsilon \psi.
\]

Let \( n(\varepsilon) \) be the density of states per unit of energy in this non-interacting system; then:

\[
T[\rho] = \int \varepsilon n(\varepsilon) \, d\varepsilon - \int \rho(r) v_{\text{eff}}(r) \, d^3r.
\]
Suppose now that \( \rho (r) \) is slightly modified by a small change \( \delta \rho \) such as to keep the total number of electrons constant; this defines an approximate density:

\[
\rho' (r) = \rho (r) + \delta \rho
\]

with:

\[
\int \delta \rho (r) \, d^3r = 0.
\]

The effective potential corresponding to \( \rho' \) is:

\[
v' (r) = v (r) + \int \frac{\rho' (r')}{|r - r'|} \, d^3r' + v_{xc} (\rho')
\]

\[
= v_{eff} (r) + \delta v.
\]

From the variational principle, the total energy does not change to first order in \( \delta \rho \):

\[
E_v [\rho] = E_v [\rho'] + O (\delta \rho)^2
\]

\[
eq T[\rho'] + \int \rho' \, v \, d^3r + \frac{1}{2} \int \frac{\rho' (r) \rho' (r')}{|r - r'|} \, d^3r' + \int \rho' \, v_{xc} (\rho') \, d^3r.
\]

Likewise, the density variation \( \delta \rho \) in the non-interacting system being made with the effective potential kept constant:

\[
E_s [\rho'] = E_s [\rho] + O (\delta \rho)^2,
\]

so that:

\[
T[\rho'] + \int \rho' \, v_{eff} \, d^3r \approx T[\rho] + \int \rho \, v_{eff} \, d^3r = \int \epsilon f \, \rho (\epsilon) \, d\epsilon
\]

and:

\[
T[\rho'] = \int \epsilon f \, \rho (\epsilon) \, d\epsilon - \int \rho' \, v_{eff} \, d^3r.
\]

From the explicit form of \( V_{eff} \), one gets:

\[
T[\rho'] + \int \rho' \, v \, d^3r = \int \epsilon f \, \rho (\epsilon) \, d\epsilon - \int \frac{\rho (r) \rho (r')}{|r - r'|} \, d^3r' -
\]

\[
- \int \rho' \, v_{xc} (\rho') \, d^3r + \int \rho' \, \delta v \, d^3r + O (\delta \rho)^2
\]

with:

\[
\delta v = \int \frac{\delta \rho (r')}{|r - r'|} \, d^3r' + \delta \rho \, \frac{\partial v_{xc} (\rho')}{\partial \rho'}.
\]

Let: \( G(\epsilon) = \left( \epsilon + \frac{\Delta}{2} - V_{eff} \right)^{-1} \) with: \( \mathrm{Im} \, \epsilon = +0 \), be the Green operator for the non-interacting system with \( V_{eff} \) and let \( G' (\epsilon) \) be the Green operator corresponding to \( v' \); they are related through the Dyson equation:

\[
G = G' - G' \, \delta v \, G
\]

\[
\approx G' - G' \, \delta v \, G'
\]

to first order in \( \delta v \).
To this approximation, the difference of the densities of states per unit of energy is:

\[ n(\varepsilon) - n'(\varepsilon) = -\frac{1}{\pi} \text{Im} \text{Tr} (G - G') = -\frac{1}{\pi} \text{Im} \text{Tr} \left( G' \delta \varepsilon G' \right) \]

Let \( N(\varepsilon) = \int \varepsilon n(\varepsilon') d\varepsilon' \) be the total number of electrons up to energy \( \varepsilon \) and let \( N' \) be the corresponding quantity for \( \varepsilon' \); to first order in \( \delta \varepsilon \):

\[ N'(\varepsilon) - N(\varepsilon) = \frac{1}{\pi} \text{Im} \text{Tr} \left( \delta \varepsilon G' \right) \]

and:

\[ \int_{\varepsilon_F}^{\varepsilon} \left[ N'(\varepsilon) - N(\varepsilon) \right] d\varepsilon = - \int \rho' \delta \varepsilon d^3r , \]

so that:

\[ \int_{\varepsilon_F}^{\varepsilon} \varepsilon n(\varepsilon) d\varepsilon + \int \rho' \delta \varepsilon d^3r = \varepsilon_F N(\varepsilon_F) - \int_{\varepsilon_F}^{\varepsilon} N'(\varepsilon) d\varepsilon \]

after integration by parts on \( \varepsilon \).

Finally:

\[ E_\text{e}[\rho] = \varepsilon_F N(\varepsilon_F) - \int_{\varepsilon_F}^{\varepsilon} N'(\varepsilon) d\varepsilon - \frac{1}{2} \int \frac{\rho'(r) \rho'(r')}{|r - r'|} d^3r d^3r' - \int \rho \frac{\partial \varepsilon_{xc}(\rho')}{\partial \rho'} d^3r . \]

3. Interaction energy of two « points defects ».

As far as the rearrangement of charge due to the interaction of the defects is small, it seems reasonable to take as approximate density \( \rho' \) the density obtained by rigid superposition of the screening charges associated with each of the defects when alone in the metal. These screening charges must be computed self-consistently beforehand for the single defects. This is far less difficult than the direct self-consistent calculation of the electronic structure of the pair of defects.

Let \( \bar{\rho}(r) \) be the electron charge density in the pure metal, \( \rho_1(r) \) that of the metal containing the first defect alone at \( \mathbf{R}_1 \), \( \rho_2(r) \) that of the metal with the second defect alone at \( \mathbf{R}_2 \) and finally, let \( \rho_{1,2}(r) \) be the unknown self-consistent electron charge density when both defects are present in the metal. Let \( Z_1 \) be the screening charge associated with the first defect, \( Z_2 \) that corresponding to the second defect. With similar indices for the total numbers of electrons, it is clear that:

\[ N_1(\varepsilon_F) - \bar{N}(\varepsilon_F) = Z_1 , \quad N_2(\varepsilon_F) - \bar{N}(\varepsilon_F) = Z_2 \]

and

\[ N_{1,2}(\varepsilon_F) - \bar{N} = Z_1 + Z_2 , \]

because one or two localized defects in an arbitrary large volume of metal cannot change the Fermi level.

The interaction energy of the defects is now defined as the difference in total energies:

\[ E_{\text{int}}(\mathbf{R}_1, \mathbf{R}_2) = E[\rho_{1,2}] - E[\bar{\rho}] - (E[\rho_1] - E[\bar{\rho}]) - (E[\rho_2] - E[\bar{\rho}]) \]

\[ = E[\rho'_{1,2}] - E[\bar{\rho}] - (E[\rho_1] - E[\bar{\rho}]) - (E[\rho_2] - E[\bar{\rho}]) + O(\delta \rho)^2 \]

with:

\[ \rho_{1,2} - \bar{\rho} = \rho_1 - \bar{\rho} + \rho_2 - \bar{\rho} . \]
As mentioned earlier in the introduction, it is illusory to attempt to compute self-consistently $\rho_1(r)$ and $\rho_2(r)$ beyond a few atomic layers around the defects. Fortunately, by virtue of the variational principle, this is not necessary. The screening charge associated with a defect being mostly localized in its atomic sphere or so, the variation of the charge integrated from the defect outwards oscillates around the value corresponding to the exact screening. There is an infinite number of closed surfaces, centered on the defect, each of them enclosing the exact screening charge while the oscillations of the density become smaller and smaller outside. It is then possible, by flattening the oscillations on the outside of such a surface, to obtain an approximate density of electron charge $\bar{\rho}_1$ valid for the calculation of the energy of the defect located at $R_1$ and, similarly, a good approximate density $\bar{\rho}_2$ for the second defect. As far as second order corrections are negligible, the interaction energy can be written in terms of the approximate densities:

$$E_{\text{int}}(R_1, R_2) = E[\bar{\rho}] - (E[\rho_1] - E[\bar{\rho}]) - (E[\rho_2] - E[\bar{\rho}])$$

with:

$$\rho_{1,2} - \bar{\rho} = \rho_1 - \bar{\rho} + \rho_2 - \bar{\rho}.$$ 

When taking into account the Coulomb repulsion between the nuclei, this leads to the following expression for the interaction energy:

$$E_{\text{int}}(R_1, R_2) = -\int_{\varepsilon_\text{F}}^\infty \left[ N_{1,2}'' - \bar{N} - (N_1' - \bar{N}) - (N_2' - \bar{N}) \right] \, d\varepsilon +$$

$$+ \frac{Z_1 Z_2}{|R_1 - R_2|} \int \frac{[\rho_1'(r) - \bar{\rho}(r)] [\rho_2'(r') - \bar{\rho}(r')]}{|r - r'|} \, d^3r \, d^3r' + \delta E_{\text{xc}}$$

with the exchange correlation correction:

$$\delta E_{\text{xc}} = -\int_{\Omega_1 \cup \Omega_2} \left( \rho_{1,2}'' \frac{\partial \varepsilon_{\text{xc}}}{\partial \rho_{1,2}''} - \bar{\rho}^2 \frac{\partial \varepsilon_{\text{xc}}}{\partial \bar{\rho}} \right) \, d^3r$$

$$+ \int_{\Omega_1} \left( \rho_1'^2 \frac{\partial \varepsilon_{\text{xc}}}{\partial \rho_1'} - \bar{\rho}^2 \frac{\partial \varepsilon_{\text{xc}}}{\partial \bar{\rho}} \right) \, d^3r + \int_{\Omega_2} \left( \rho_2'^2 \frac{\partial \varepsilon_{\text{xc}}}{\partial \rho_2'} - \bar{\rho}^2 \frac{\partial \varepsilon_{\text{xc}}}{\partial \bar{\rho}} \right) \, d^3r ,$$

$\Omega_1$ and $\Omega_2$ being the volumes kept around each defect and in which, respectively, $\rho_1'$ or $\rho_2'$ differ from $\bar{\rho}$.

Usually, the electronic charge density changes produced by a defect on the outside of its own atomic cell are rather weak, typically of the order of one tenth or even one hundredth of a unit of charge per atomic cell. Under these conditions, it is permissible to linearize the corresponding change in exchange and correlation energy. The exchange and correlation correction disappears then to first order, except in the atomic cells $\sigma_1$ and $\sigma_2$ of the defects and one is left with:

$$\delta E_{\text{xc}} = -\int_{\sigma_1} \left( \rho_1' - \bar{\rho} \right) \left[ \rho_1' \frac{\partial}{\partial \rho_1'} v_{\text{xc}}(\rho_1) - \bar{\rho} \frac{\partial}{\partial \bar{\rho}} v_{\text{xc}}(\bar{\rho}) \right] \, d^3r$$

$$-\int_{\sigma_2} \left( \rho_2' - \bar{\rho} \right) \left[ \rho_2' \frac{\partial}{\partial \rho_2'} v_{\text{xc}}(\rho_2) - \bar{\rho} \frac{\partial}{\partial \bar{\rho}} v_{\text{xc}}(\bar{\rho}) \right] \, d^3r$$

$$= \int_{\varepsilon_\text{F}}^\infty \left[ \delta N_{1,2}^{\text{xc}}(\sigma_1) - \delta N_{1,2}^{\text{xc}}(\sigma_1) \right] \, d\varepsilon + \int_{\varepsilon_\text{F}}^\infty \left[ \delta N_{1,2}^{\text{xc}}(\sigma_2) - \delta N_{1,2}^{\text{xc}}(\sigma_2) \right] \, d\varepsilon ,$$
where $\delta N^\text{exc}_i(\sigma_2)$ is the contribution to $N^\prime_i$ of the change in the exchange-correlation potential in $\sigma_2$ with respect to the pure metal, and similar meaning for the other terms. So, the exchange-correlation correction $\delta E_{\text{xc}}$ completely drops out provided that the exchange and correlation modifications of the potentials are not made. This means that $N^\prime_1$ and $N^\prime_2$ should be computed with the full potential, exchange and correlation included, in the atomic cells of the defects, but with only the Hartree-like Coulomb corrections with respect to the pure metal in $\Omega_1 - \sigma_1$ and $\Omega_2 - \sigma_2$ respectively. From the linearity of the relation between electric charge and Coulomb potential, the perturbative potential $V_{1,2}^{\prime\prime}$ of the pair of defects in which $N_{1,2}^\prime$ must be computed is just the sum:

$$V_{1,2}^{\prime\prime}(\mathbf{r}) = V_1^\prime(\mathbf{r}) + V_2^\prime(\mathbf{r})$$

of the perturbative potentials in which $N^\prime_1$ and $N^\prime_2$ are calculated. These potentials, constructed as explained above, are not self-consistent and do not attract the exact screening charge, but they must give the correct interaction energy according to the final formula:

$$E_{\text{int}} = - \int_{\epsilon_{\text{F}}}^{\epsilon_{\text{F}}} \left[ (N_{1,2}^{\prime\prime} - \bar{N}) - (N_1^\prime - \bar{N}) - (N_2^\prime - \bar{N}) \right] \text{d}\epsilon + \frac{Z_1 Z_2}{|\mathbf{R}_1 - \mathbf{R}_2|}$$

$$- \int \frac{[\rho_1^\prime(\mathbf{r}) - \bar{\rho}(\mathbf{r})] [\rho_2^\prime(\mathbf{r}') - \bar{\rho}(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|} \text{d}^3r \text{d}^3r'$$

in which the last integral represents the Coulomb interaction of the two screening electron clouds which is counted twice in the one-electron part.

The one-electron integral can be written in terms of the Green operator $\bar{G}$ for the pure metal, and those corresponding respectively to $V_1^\prime$, $V_2^\prime$ and $V_{1,2}^{\prime\prime}$. From the Dyson equation:

$$G_1^\prime = \bar{G} + \bar{G}V_1^\prime G_1^\prime$$

and similar relations with $V_2^\prime$ and $V_{1,2}^{\prime\prime}$, one gets for two spin directions:

$$N_1^\prime(\epsilon) - \bar{N}(\epsilon) = - \frac{2}{\pi} \text{Im log} (\bar{G}G_1^\prime)$$

$$= - \frac{2}{\pi} \text{Arg Det} (1 - \bar{G}V_1^\prime)$$

so that:

$$- \int_{\epsilon_{\text{F}}}^{\epsilon_{\text{F}}} \left[ (N_{1,2}^{\prime\prime} - \bar{N}) - (N_1^\prime - \bar{N}) - (N_2^\prime - \bar{N}) \right] \text{d}\epsilon =$$

$$= \frac{2}{\pi} \int_{\epsilon_{\text{F}}}^{\epsilon_{\text{F}}} \text{Arg Det} \left[ \frac{(1 - \bar{G}(V_1^\prime + V_2^\prime))}{(1 - \bar{G}V_1^\prime) (1 - \bar{G}V_2^\prime)} \right] \text{d}\epsilon ;$$

the determinant can be factorized in a way appropriate for numerical calculation.

Let us take for illustration the simple model of a single tight-binding band with two perfectly screened impurity atoms, one at the origin: $\mathbf{R}_1 = 0$ and the second at $\mathbf{R}_2 = \mathbf{R}$:

$$\langle 0 | V_1^\prime | 0 \rangle = V_1^\prime, \quad \langle \mathbf{R} | V_2^\prime | \mathbf{R} \rangle = V_2^\prime,$$
all other matrix elements being zero. In this model, the corrective term disappears because
the localized screening charges neutralize exactly the nuclear terms and one is left with the
one-electron contribution:

\[
\delta E_{\text{int}} = \frac{2}{\pi} \int_{\varepsilon_F}^{\varepsilon_F} \text{Arg} \det \frac{1 - \bar{G} V_1 - \bar{G} V_2}{(1 - \bar{G} V_1) (1 - \bar{G} V_2)} \, d\varepsilon = \frac{2}{\pi} \int_{\varepsilon_F}^{\varepsilon_F} \text{Arg} \left[ 1 - \frac{V_1 V_2 \langle 0 \mid \bar{G} \mid R \rangle^2}{(1 - \langle 0 \mid \bar{G} \mid 0 \rangle V_1) (1 - \langle 0 \mid \bar{G} \mid 0 \rangle V_2)} \right] \, d\varepsilon.
\]

In lowest order in perturbation, this gives:

\[
\delta E_{\text{int}} \approx -2 \frac{V_1 V_2}{\pi} \int_{\varepsilon_F}^{\varepsilon_F} \text{Im} \langle 0 \mid \bar{G} \mid R \rangle^2 \, d\varepsilon.
\]

In the limit of large \( R \), with a free electron approximation for the dispersion law in the band:

\[
\langle 0 \mid \bar{G} \mid R \rangle \approx -\frac{V_{\text{at}}}{2\pi} e^{i k R} / R
\]

\( k \) being the electron wave vector and \( v_{\text{at}} \) the atomic volume, one recovers the asymptotic
behaviour of the linear response theory:

\[
E_{\text{int}} \sim \frac{V_1 V_2}{4\pi} v_{\text{at}} n_{\text{at}}(\varepsilon_F) \cos \frac{2 k_F R}{R^3}
\]

with \( n_{\text{at}}(\varepsilon_F) \) being the density of electron states per atom and unit of energy.

4. Discussion.

In the ideal case where each defect is perfectly screened in its own atomic cell, the Coulomb
interaction of the screening clouds compensates the nuclear repulsive term in the atomic
sphere approximation so that the corrective term disappears totally, except for high order
multipolar terms which must be very small in compact crystalline structures. \( E_{\text{int}} \) is then
given by the one electron contribution alone. It is clear in that case that the interaction energy
results from the multiple scattering of the conduction electrons by the pair of screened,
therefore neutral, defects and is not given by the product of the ionic charge of one of them in
the Coulomb potential created by the other one on its site. A similar remark was already
made by Caroli [13] for the coupling between the localized magnetic moments associated with
two virtual bound states. One should not forget that the screened potential of an impurity
atom is not weak in its own cell; it may give rise to resonances or even subtract bound states
out of the conduction band; only on the outside of this cell can it be considered as a small
perturbation.

In many real cases, the defect is under-screened in its own atomic cell and the screening
charge involves its neighbouring atoms. This is so, for instance, for vacancies in metals or
metallic compounds such as FeAl [14]. The conduction electrons tunnel easily through the
vacancies which in some cases can retain up to one electron charge which has to be borrowed
from the neighbouring atoms. In such cases, the volume \( \Omega \) of the cluster to be treated self-
consistently must include at least the first nearest neighbour shell. When the defects are close
enough so that their screening charges overlap, the corrective term becomes important. It is
then essential that each individual cluster be neutral in order to avoid errors much larger than the correction itself.

In order to illustrate the influence of the overlap of the screening charges when no cut-off is made on the oscillations, we have calculated the Coulomb interaction energy correction $\delta E(R)$ for two defects at a distance $R$ apart, each defect being simulated by a hard-core pseudo-potential of radius $a$ repelling exactly one electron in the « s » partial waves of a free electron gas (Fig. 1). From the screening condition for the individual defects, one has: $2 k_F a = \pi$, so that $k_F = 1$ a.u. would give $a = \frac{\pi}{2}$ a.u. while the atomic radius would be: $r_s \approx 1.92$ a.u. On the same picture are plotted the potential energy $V(R)$ for an electron at distance $R$ from a single screened defect and the screening charge: $Q(R) = 4 \pi \int_0^R \rho(r) r^2 dr$ inside a sphere of radius $R$. One sees that $\delta E(R)$ becomes rapidly much smaller than $V(R)$ but in order to get a correct result when the two defects are but a few atomic distances apart, it is necessary to integrate up to about one hundred times the radius in which the right screening charge $Q = -1$ is obtained for the first time. Moreover, if one puts a cut-off on the radius of the sphere in which the screening charge $Q(r)$ is taken into account, then the

Fig. 1. — Coulomb correction to the interaction energy of two defects in a free electron gas, versus the distance separating these defects: $a$: radius of the hard-core pseudopotentials; $Q(R)$: screening charge inside a sphere of radius $R$ for one defect (-----); $V(R)$: potential energy of one electron at a distance $R$ of one screened defect (-----); $\delta E(R)$: total interaction energy correction for two screened defects separated by a distance $R$ (-----).
numerical calculation shows that the error made on $\delta E(R)$ may be more than one order of magnitude larger than the value $\delta E(R)$ to be computed if $Q(r)$ is not equal to $-1$. This is not the case when $Q(r) = -1$.

The obvious conclusion is that the one-electron scattering potential and the correction for electron-electron interactions must be treated simultaneously and coherently with great care if one wants to get significant quantitative results from a numerical calculation.

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