About the screening of the charge of a proton migrating in a metal

A. Lodder
Faculty of Sciences/Natuurkunde en Sterrenkunde,
Vrije Universiteit De Boelelaan 1081,
1081 HV Amsterdam, The Netherlands
(Dated: June 8, 2018)

The amount of screening of a proton in a metal, migrating under the influence of an applied electric field, is calculated using different theoretical formulations. First the lowest order screening expression derived by Sham is evaluated. In addition ‘exact’ expressions are evaluated which were derived according to different approaches. For a proton in a metal modeled as a jellium the screening appears to be $15 \pm 10\%$, which is neither negligible nor reconcilable with the controversial full-screening point of view of Bosvieux and Friedel. In reconsidering the theory of electromigration, a new simplified linear-response expression for the driving force is shown to lead to essentially the same result as found by Sorbello, who has used a rather complicated technique. The expressions allow for a reduction such that only the scattering phase shifts of the migrating impurity are required.

Finally it is shown that the starting formula for the driving force of Bosvieux and Friedel leads exactly to the zero-temperature limit of well-established linear response descriptions, by which the sting of the controversy has been removed.

I. INTRODUCTION

The amount of screening of a hydrogen atom in a current carrying metal has been the subject of a long-standing controversy. In brief, considering the driving force $F$ on such an atom as being composed of two contributions, a direct force $F_d$ due to the charge of the proton and a wind force $F_w$ due to transfer of momentum of the current carrying electrons to the proton, so

$$F = F_d + F_w = (Z_d + Z_w) eE = Z^* eE,$$  \hspace{1cm} (1)

Bosvieux and Friedel found a complete cancellation of $F_d$, implying full screening of the proton charge and only a wind force being operative, while most other researchers in the field were in favor of at most a very limited screening. According to the convention in electromigration theory, the forces in Eq. (1) are written as being proportional to corresponding valences and the applied electric field $E$. The effective valence $Z^*$ is the measurable quantity. The wind force has been calculated reliably for many systems with ab initio methods for the electronic structure. This has been done not only for migration of interstitials such as hydrogen, but also for substitutional impurities, including self-electromigration.

In view of the long history of the controversy regarding the direct force we mention just a few key papers. The linear response expression for the driving force derived by Kumar and Sorbello was considered as a sound starting point for the resolution of the controversy. From an evaluation to lowest order in the impurity potential Sham concluded to a negligible screening. Using an evaluation up to all orders in the potential, in 1985 Sorbello found a screening of at most 25\%. This result, combined with a measurement of negligible screening in V(H) and Ta(H) and a screening of the order of 50\% in Nb(H), led to a consensus. Nevertheless, Friedel kept defending that only a wind force was operative, the more so as Turban et al. had given another support for that point of view. The confusing feature of the latter work is that their starting formula is a well-established form of a linear response expression. However, these authors do not evaluate that expression, but they use a proportionality argument regarding the expression for another physical quantity. Another support for the full-screening point of view was given by the present author. However, that result was considered to be valid in the low temperature limit only, and this limit is a rather academic one in view of the relatively high temperatures at which electromigration experiments are carried out. More recently Ishida predicted a screening ranging from 0 to 100\%, but his results were depending sensitively on the electron density of the host metal.

We will present a thorough study of the amount of screening. After summarizing the main ingredients of the linear response description of the driving force in this is done by first evaluating Sham’s screening expression numerically for a number of model potentials representing the impurity. The results, given in do not support Sham’s conclusion of a negligible screening, but they are in line with Sorbello’s result of a screening of 10-30\%.

Secondly, in we will present a very simple evaluation of the linear response description. This evaluation is supplementary to the evaluation given by Rimbey and Sorbello and furthermore much more straightforward. The
two descriptions are compared in §V. In §VI it appears to be possible to reduce the final expression for the direct force valency \( Z_d \) to a form containing just the scattering phase shifts of the migrating impurity potential. Numerical results will be presented in §VII, and compared with Sorbello’s results.3

Finally, in §VIII we will show that the starting expression of Bosvieux and Friedel for the driving force is precisely the zero temperature limit of well-established linear response expressions. This is found by describing the switch-on of the electric field properly and by giving credit to the hermitian property of the Hamiltonian of the unperturbed system.

II. LINEAR-RESPONSE DESCRIPTION

The linear response expression for the force on an impurity with chemical valency \( Z_i \) at a position \( \mathbf{R}_1 \) due to an applied electric field is given by

\[
F = Z_i e E - ie E \nu \int_0^\infty dt e^{-\alpha t} \text{Tr} \left\{ \rho(H) \left[ F_{\text{op}}(t), \sum_j r_{j\nu}^\nu \right] \right\} \equiv F_{d}^{\text{bare}} + F_{\text{total}}^{w}.
\] (2)

The first term clearly is the direct force on the bare ion. The cartesian label \( \nu \) runs from 1 to 3, the infinitesimal positive number \( a \) represents the adiabatical switch-on of the electric field represented by the potential

\[
\delta V(t) = e E e^{\alpha t} \cdot \left( \sum_j r_j - Z_i \sum_\alpha \mathbf{R}_\alpha \right) \equiv \delta V e^{\alpha t},
\] (3)

with \( j \) running over the electrons and \( \alpha \) over the ions, and the operator \( \rho(H) \) is the grandcanonical density depending on the system Hamiltonian \( H \). The force operator contains the electron-impurity potential

\[
V_{ei} = \sum_{j,\alpha} v(r_j - \mathbf{R}_\alpha) \equiv \sum_{j,\alpha} v_{\alpha j}^\alpha,
\] (4)

which is part of the system Hamiltonian, and is given by

\[
F_{\text{op}} \equiv -\nabla_{\mathbf{R}_1} V_{ei} = -\sum_j \nabla_{\mathbf{R}_1} v(r_j - \mathbf{R}_1) \equiv \sum_j f_{1j}.
\] (5)

Its time dependence refers to the Heisenberg representation

\[
F_{\text{op}}(t) \equiv e^{iHt} F_{\text{op}} e^{-iHt}.
\] (6)

It appears that the second term in Eq. (2), which is of course supposed to lead to the wind force, also contains some screening contribution to the direct force. The controversy has not to do with the fact that there is a screening contribution in \( F_{\text{total}}^{w} \), but it is as to the magnitude of that screening contribution that people don’t agree. The expression published by Kumar and Sorbello,9

\[
F_{\text{total}}^{w} = -\frac{i}{a} e E \nu \int_0^\infty dt e^{-\alpha t} \text{Tr} \left\{ \rho(H) \left[ F_{\text{op}}(t), J_{\nu} \right] \right\},
\] (7)

follows simply and straightforwardly from a partial integration of Eq. (2) with respect to the time. The current vector is defined as

\[
\mathbf{J} = ie \left( \sum_j r_j, H \right) = -e \sum_j \frac{p_j}{m} = \sum_j \mathbf{j}_j.
\] (8)

The driving force (2) can be decomposed as follows:

\[
F = Z_i e E + F_{\text{total}}^{w} = Z_i e E + F_{\text{scr}}^{w} + F_{\text{BF}}^{w} = (Z_i + Z_{\text{scr}}^{w} + Z_{\text{w}}) e E = (Z_d + Z_{\text{w}}) e E,
\] (9)

containing the result of Bosvieux and Friedel for the wind force \( F_{\text{BF}}^{w} \) and a screening contribution2. In all treatments available \( F_{\text{BF}}^{w} \) can be written in its general form

\[
F_{\text{BF}}^{w} = -\int \delta n(\mathbf{r}) \nabla_{\mathbf{R}_1} v^1 d^3 r, \quad \text{with} \quad v^1 = v(r - \mathbf{R}_1).
\] (10)
The precise explicit form depends on the level of approximation used to represent $\delta n(\mathbf{r})$, which is the local deviation of the electron density from its unperturbed host value due to the applied field and the presence of the impurity. From now on we will concentrate on $Z_4$.

All previous relevant descriptions have been given for the electron-impurity system, for which the Hamiltonian $H$ can be written as a sum of single particle Hamiltonians $h$, so

$$ H = \sum_j h^j \quad \text{with} \quad h = h_0 + v = h_0 + \sum_a e^{\alpha a}. \quad (11) $$

This allows for a reduction of the many body expression in Eq. (12) to the following single particle expression,

$$ F_w^{\text{total}} = -ie E_\nu \int_0^\infty dt \ e^{-\alpha t} \ tr\left\{[r^\nu, n(h)]f^1(t)\right\}, \quad (12) $$

where $n(h)$ is the Fermi-Dirac distribution function in operator form

$$ n(h) = \frac{1}{e^{\beta(h-v_F)} + 1}. \quad \quad (13) $$

It has been shown explicitly that if in the right hand side of Eq. (12) the statistical operator is replaced by this operator for the free particle system, so $n(h) \to n(h_0)$, the Bosvieux-Friedel wind force expression $F_w^{\text{BF}}$ arises. That means that the screening part is given by

$$ F_w^{\text{scr}} = -ie E_\nu \int_0^\infty dt \ e^{-\alpha t} \ tr\left\{[r^\nu, n(h) - n(h_0)]f^1(t)\right\} = Z^{\text{scr}} e E. \quad (14) $$

The screening valency $Z^{\text{scr}}$ is defined as

$$ Z^{\text{scr}} = -i \frac{3}{3} \int_0^\infty dt \ e^{-\alpha t} \ tr\left\{[\mathbf{r}, n(h) - n(h_0)] \cdot f^1(t)\right\}, \quad (15) $$

in which the factor of $\frac{1}{3}$ comes from the fact that all three terms in the inner product of the vectors $\mathbf{r}$ and $f^1$ contribute equally. In all further evaluations the metallic host is modeled by a jellium, which is the only model used so far in the literature for the study of the direct force problem. This means that the electrons are perturbed by the random distribution of impurities only. Following Sham we now first consider the result to lowest (second) order in the impurity potential $v$.

### III. Evaluation of Sham’s Expression

The evaluation of Eq. (15) to lowest order in $v$ requires the expansion of the statistical operator $n(h) - n(h_0)$ in $v$,

$$ n(h) = n(h_0) - n(h) \int_0^\beta ds \ e^{sh} \ e^{-sh_0} (1 - n(h_0)), \quad (16) $$

while in the time dependence of $f^1$ one can replace $h$ by $h_0$. One obtains

$$ Z^{\text{scr}} = \frac{4}{3m} \sum_{kk'} (k^2 - k \cdot k') \frac{|v_{kk'}|^2}{(\epsilon_k - \epsilon_{k'})^2 + a^2} \left( \frac{\partial n_k}{\partial \epsilon_k} - \frac{n_k - n_{k'}}{\epsilon_k - \epsilon_{k'}} \right), \quad (17) $$

where $k$ is a free electron wave vector and $\epsilon_k$ is the corresponding energy. The matrix element $< k|v^{\nu}, n(h) - n(h_0)|k' >$ is most easily evaluated if one realizes, that it is equal to $i(\frac{\partial}{\partial \epsilon_k} + \frac{\partial}{\partial \epsilon_{k'}}) < k|n(h) - n(h_0)|k' >$. Following Sham and Sorbello the potential $v$ refers to the migrating impurity only. Sham stored part of the presence of the impurities through the replacement $a \to \tau^{-1}$, $\tau$ being the transport relaxation time due to the impurities, which can be justified by an average over the distribution of the impurities in the time dependence of the force operator. Both Sham and Sorbello were able to make their complete derivations after taking the $T \to 0$ limit only. It has been shown that Eq. (17) reduces to Sham’s expression after taking that limit $\Delta$. A numerical evaluation of $Z^{\text{scr}}$ becomes possible if one employs the spherical wave expansion for a plane wave, converts the summations over the wave vectors to integrals and carries out the angular integrals over the directions of the wave vectors. After using the relation between $k^2$ and the energy $\epsilon_k$ one ends up at

$$ Z^{\text{scr}} = \frac{4}{3\pi^2 m} \int_0^\infty d\epsilon_k \int_0^\infty d\epsilon_{k'} \left( \frac{\partial n_k}{\partial \epsilon_k} - \frac{n_k - n_{k'}}{\epsilon_k - \epsilon_{k'}} \right) \sum_\ell f_\ell(k, k'), \quad (18) $$
in which the function \( f_\ell(k, k') \) is defined as

\[
f_\ell(k, k') = \varepsilon_k \sqrt{\varepsilon_{k'}} \varepsilon_{k'} v_\ell(k', k) \left[ (2\ell + 1)k v_\ell(k', k) - 2(\ell + 1)k' v_{\ell+1}(k', k) \right],
\]

containing the information about the ion potential through

\[
v_\ell(k', k) = \int_0^\infty r^2 dr j_\ell(k' r) v(r) j_\ell(k r).
\]

The integrand has to be treated with care when \( \varepsilon_{k'} = \varepsilon_k \), because then the denominator attains the value \( a^2 \) which would imply 'singular' behaviour. However, precisely then the numerator becomes zero, because \( \lim_{\varepsilon_{k'} \to \varepsilon_k} (n_k - n_{k'})/(\varepsilon_k - \varepsilon_{k'}) \to \partial n_k / \partial \varepsilon_k \). The crucial part of the integrand lies in the square around the point \((\varepsilon_k, \varepsilon_{k'}) = (\varepsilon_F, \varepsilon_F)\). In studying the \( Z_{\text{scr}} \) integral it appears that in that square one has to keep the Fermi-Dirac distribution function in its finite temperature form. We could not obtain a reliable stable numerical result by using Sham’s \( T \to 0 \) expression.

The result of a numerical evaluation for different ion potentials is shown in FIG. 1. We used a screened Coulomb potential

\[
v(r) = -\frac{Z_i e^2 e^{-\lambda r}}{r} \quad \text{while} \quad v_{k'k} = \frac{1}{8\pi^3} \int d^3r \ e^{i(k-k') \cdot r} v(r),
\]

with \( Z_i = 1 \) representing a proton in a jellium and the inverse screening length \( \lambda \) given by the Thomas-Fermi expression.\(^19\)

\[
\lambda^2 = 4\pi e^2 N(\varepsilon_F) \quad \text{with} \quad N(\varepsilon) = \frac{m\sqrt{2m\varepsilon}}{\pi^2} \to v_{kk} = -\frac{Z_i}{8\pi^3 N(\varepsilon_F)}.
\]

In addition square well potentials were employed in the same spirit as Sorbello did.\(^3\) The width \( r_0 \) of the square well potential was chosen to be equal to the screening length \( 1/\lambda \) and twice as large. The corresponding well depth \( v_0 \) was determined by the condition \( v_0/v_c = 0.999 \), where \( v_c = \pi^2/8mr_0^2 \) is the critical value of the well depth for which a bound state forms. For further details, see Ref.\(^3\). The value of \( \lambda \) is determined by the Fermi energy. While Sorbello chose five values for the Fermi energy, typical for metals ranging from sodium to aluminum, we have done the calculation for a whole range of Fermi energies. The results are plotted as a function of the Fermi wave number \( k_F \). The \( k_F \) values of sodium and aluminum are indicated.

FIG. 1: The amount of screening represented by \( Z_{\text{scr}} \) according to Eq. \( 18 \), for the screened Coulomb potential and for two square well potentials.

---

\(^1\) The integrand has to be treated with care when \( \varepsilon_{k'} = \varepsilon_k \), because then the denominator attains the value \( a^2 \) which would imply 'singular' behaviour. However, precisely then the numerator becomes zero, because \( \lim_{\varepsilon_{k'} \to \varepsilon_k} (n_k - n_{k'})/(\varepsilon_k - \varepsilon_{k'}) \to \partial n_k / \partial \varepsilon_k \). The crucial part of the integrand lies in the square around the point \((\varepsilon_k, \varepsilon_{k'}) = (\varepsilon_F, \varepsilon_F)\). In studying the \( Z_{\text{scr}} \) integral it appears that in that square one has to keep the Fermi-Dirac distribution function in its finite temperature form.

The result of a numerical evaluation for different ion potentials is shown in FIG. 1. We used a screened Coulomb potential

\[
v(r) = -\frac{Z_i e^2 e^{-\lambda r}}{r} \quad \text{while} \quad v_{k'k} = \frac{1}{8\pi^3} \int d^3r \ e^{i(k-k') \cdot r} v(r),
\]

with \( Z_i = 1 \) representing a proton in a jellium and the inverse screening length \( \lambda \) given by the Thomas-Fermi expression.\(^19\)

\[
\lambda^2 = 4\pi e^2 N(\varepsilon_F) \quad \text{with} \quad N(\varepsilon) = \frac{m\sqrt{2m\varepsilon}}{\pi^2} \to v_{kk} = -\frac{Z_i}{8\pi^3 N(\varepsilon_F)}.
\]

In addition square well potentials were employed in the same spirit as Sorbello did.\(^3\) The width \( r_0 \) of the square well potential was chosen to be equal to the screening length \( 1/\lambda \) and twice as large. The corresponding well depth \( v_0 \) was determined by the condition \( v_0/v_c = 0.999 \), where \( v_c = \pi^2/8mr_0^2 \) is the critical value of the well depth for which a bound state forms. For further details, see Ref.\(^3\). The value of \( \lambda \) is determined by the Fermi energy. While Sorbello chose five values for the Fermi energy, typical for metals ranging from sodium to aluminum, we have done the calculation for a whole range of Fermi energies. The results are plotted as a function of the Fermi wave number \( k_F \). The \( k_F \) values of sodium and aluminum are indicated.
FIG. 2: \( v_{kk}^2 \) plotted as a function of \( k_F \), for the two square well potentials and the screened Coulomb potential.

Because \( \lambda \) increases monotonically with the Fermi energy, the range of the corresponding screened Coulomb potential decreases with increasing \( k_F \), which reduction in strength is seen clearly in the solid curve. In FIG. 2 the \( v_{kk}^2 \) curves are plotted for the three potentials. A clear decrease is seen for the Coulomb potential, and a rather flat behaviour for the square well potentials, while the one with \( 2/\lambda \) is markedly stronger than the one with the smaller width. Apparently, the screening to second order in the impurity potential is not negligible at all, but on the average as large as 15 \( \pm \) 10\%. As a guide for the eye we gave the average of \( Z_{\text{scr}} \) for the three potentials as a dotted line.

For security we evaluated an alternative expression for \( Z_{\text{scr}} \), given by

\[
Z_{\text{scr}} = -\frac{4}{3m} \sum_{kk'} (k^2 - k \cdot k') v_{kk'} \left( \frac{\epsilon_k - \epsilon_{k'}}{\epsilon_k - \epsilon_{k'}} \right)^2 a^2 \left( \frac{(\epsilon_k - \epsilon_{k'})^2}{(\epsilon_k - \epsilon_{k'})^2 + a^2} \right)^2 .
\]

(23)

This expression follows if Eq. (15) is modified such, that the dipole operator \( r \) commutes with the force operator \( f_1(t) \) instead of with the statistical operator. While \( Z_{\text{scr}} \) given by Eq. (17) reduces to Sham’s expression after taking the \( T \rightarrow 0 \) limit, such a proof is not available for \( Z_{\text{scr}} \) given by Eq. (23). On the other hand, the two expressions (17) and (23) are equivalent, being related to each other through a partial integration for the derivatives with respect to the \( k \) and \( k' \) vectors. The alternative for Eq. (18) becomes

\[
Z_{\text{scr}} = -\frac{4}{3\pi^2 m} \int_0^\infty dk \int_0^\infty dk' \frac{n_k - n_{k'}}{\epsilon_k - \epsilon_{k'}} \left( \frac{(\epsilon_k - \epsilon_{k'})^2}{(\epsilon_k - \epsilon_{k'})^2 + a^2} \right)^2 \sum_\ell f_\ell(k,k').
\]

(24)

If one takes proper care of the higher sensitivity of the expression (24) to the choice of the infinitesimal parameter \( a \) the results turn out to be the same. It can be taken relatively small, much smaller than a typical value of 0.01 for the inverse transport relaxation time. In fact, it is the mesh of the integration that determines the lower limit of \( a \). For the expressions (18) and (24) it was never larger than 0.00015 and 0.005 respectively. On the other hand, for \( a = 0.01 \) the screening represented by the curves in FIG. 1 reduces by at most 2\%.

IV. REDUCTION OF LINEAR-RESPONSE FORMULA FOR THE SCREENING

The evaluation of the linear-response formula (15) to all orders in the impurity potential can be achieved by restricting the evaluation to a system with one impurity in a jellium, which is in accordance with earlier work by others. In that case \( f_1 = i[\mathbf{p},\mathbf{h}] = i[\mathbf{p},h_0 + \mathbf{v}] \). By writing Eq. (15) in terms of eigenstates of \( h \rightarrow h_0 + \mathbf{v} \), labeled by \( q \) and \( q' \), one can carry out the time integral and finds

\[
Z_{\text{scr}} = \frac{i}{3} \sum_{qq'} <q| [\mathbf{r}, n(h) - n(h_0)] |q'> \cdot \frac{\epsilon_q - \epsilon_{q'}}{\epsilon_{q'} - \epsilon_q + ia} \mathbf{p}_{q'q}.
\]
\[ = \frac{i}{3} \sum_{qq'} <q||r,n(h) - n(h_0)||q'> \cdot \left(-1 + \frac{ia}{\epsilon_{q'} - \epsilon_q + ia}\right) p_{q'q} = \]

\[ - \frac{i}{3} \text{tr}\{[r,n(h) - n(h_0)] \cdot p\} + \frac{i}{3} \sum_{qq'} <q||r,n(h) - n(h_0)||q'> \cdot p_{q'q}. \]

The first term in the last line reduces to \(-Z_i\) because \(i \text{ tr}\{[r',n(h) - n(h_0)]p^0\} = i \text{ tr}\{(n(h) - n(h_0)) [p^0, r']\} = \text{ tr}\{(n(h) - n(h_0)) \delta_{\nu,\mu} = Z_i \delta_{\nu,\mu}.\) One arrives at

\[ Z^{\text{corr}} = -Z_i + Z_\text{corr} \quad \text{with} \quad Z_\text{corr} = \frac{i}{3} \sum_{qq'} <q||r,n(h) - n(h_0)||q'> \cdot p_{q'q}. \]

In view of Eq. (19) this would imply a correction term \(Z_\text{corr} = Z_\text{d} \) to the cancellation of the bare direct valency \(Z_i\). The step of subtracting and adding an \(ia\) term in the numerator in the second line of Eq. (26) may look somewhat artificial, and the \(ia\) factor creates the impression to lead to a zero result in the \(a \to 0\) limit. But in following Sorbello it is seen in the third line that for the \(\epsilon_q = \epsilon_{q'}\) terms the \(ia\) factor cancels, and the remaining terms give a finite contribution.\(^{20}\)

Sorbello\(^3\) starts from a result obtained by Rimbey and Sorbello\(^{36}\) through an evaluation of Eq. (7) and finds after some rewritings for \(Z_\text{d}\)

\[ Z_\text{d} = -\frac{2}{3 \pi m} \text{Im tr}\{p^2 (G(\epsilon_F) - G^0(\epsilon_F))\}. \]

The single particle Green’s function \(G(\epsilon)\) for one impurity in a jellium, with \(h = h_0 + v^1\), and the free electron Green’s function \(G^0(\epsilon)\) are given by

\[ G(\epsilon) = \frac{1}{\epsilon + ia - h} \quad \text{and} \quad G^0(\epsilon) = \frac{1}{\epsilon + ia - h_0} \quad \text{with} \quad h_0 = \frac{p^2}{2m}. \]

This form for \(Z_\text{d}\) is Sorbello’s Eq. (12) and it implies a cancellation of \(Z_i\) present in his Eq. (7). In order to distinguish our result for \(Z_\text{d}\) from Sorbello’s \(Z_\text{d}\) we keep the notation \(Z_\text{corr}\).

V. COMPARISON OF THE TWO DESCRIPTIONS

While the description by Rimbey and Sorbello is rather involved and the result \(^{24}\) is obtained in a few lines, it is worth while to compare the final expressions. We first evaluate \(Z_\text{corr}\) to lowest order in the impurity potential, for which we take a screened Coulomb potential, Eq. \(^{24}\). By using Eq. (10) and the equality

\[ [r,n(h)] = -\frac{i}{m} \int_0^\beta ds n(h)e^{sh}pe^{-sh} (1 - n(h)), \]

in which the electron mass \(m = \frac{1}{2}\) in atomic units, one finds straightforwardly for \(Z^{\text{corr}}_\text{d}\)

\[ Z^{\text{corr}}_\text{d} = \frac{i}{3} \sum_k <k||r,n(h) - n(h_0)||k > \cdot k = -4\pi \sqrt{\epsilon_F} v_{kk} = Z_i \equiv Z_i(\text{pot}), \]

in which a quantity \(Z_i(\text{pot}) = -4\pi \sqrt{\epsilon_F} v_{kk}\) is defined to be used below. For the screened Coulomb potential this quantity is equal to \(Z_i = 1\), but this is not the case for other potentials. This result from an explicit calculation follows also if one writes the sum over the free space states \(|k\rangle\) as a trace and uses the equality given in the sentence just below Eq. (26).

Similarly one finds for Sorbello’s \(Z_\text{d}\) to lowest order in the impurity potential, writing the trace in Eq. (26) in terms of free space states labeled by \(k\),

\[ Z^{(0)}_\text{d} = -\frac{2}{3 \pi m} \text{Im} \int d^3 k k^2 G^0_k(\epsilon_F)v_{kk}G^0_k(\epsilon_F) = -4\pi \sqrt{\epsilon_F} v_{kk} = Z_i. \]

This is obtained by using the following two equalities,

\[ \frac{\partial}{\partial \epsilon_k} G^0_k(\epsilon) = \frac{\partial}{\partial \epsilon_k} \frac{1}{\epsilon - \epsilon_k + ia} = G^0_k(\epsilon) G^0_k(\epsilon) \quad \text{and} \quad \lim_{a \to 0} \text{Im} G^0_k(\epsilon_F) = -\pi \delta(\epsilon_F - \epsilon_k). \]
Apparently, to lowest order in the impurity potential the two final expressions \( Z_{\text{corr}} \) and \( Z_4 \) are equal and they reproduce the bare valency of the migrating ion. Although the complete expressions are not equal, an ‘almost’ equality can be derived. We rewrite \( Z_{\text{corr}} \) by applying Eq. (24) both for \( h \) and \( h_0 \). After inserting a complete set of free electron states in the \( h_0 \) term in Eq. (24) and carrying out the integral over \( s \), one finds

\[
Z_{\text{corr}} = \frac{\beta}{3m} \sum_{qq'} \left( n_q (1 - n_q) p_{qq'} - \sum_{k''} n_{k''} (1 - n_{k''}) < q | k'' > k'' | q' > \right) \cdot p_{q'q}
\]

\[
\to - \frac{1}{3\pi m} \sum_{qq'} \left( \text{Im}G_q(\epsilon_F)p_{qq'} - \sum_{k''} \text{Im}G_{k''}(\epsilon_F) < q | k'' > k'' | q' > \right) \cdot p_{q'q}
\]

\[
= - \frac{1}{3\pi m} \sum_{qq'} < q | p \left( G(\epsilon_F) - G^0(\epsilon_F) \right) | q' > \cdot p_{q'q}. \tag{33}
\]

In the transition from the first to the second line the \( T \to 0 \) limit was taken, for which \( \beta n_q (1 - n_q) = -\frac{\partial}{\partial q} n_q \to \delta(\epsilon_q - \epsilon_F) = -\frac{1}{\pi} \text{Im}G_q(\epsilon_F) \). Both Sham and Sorbello give their elaborated expressions in this \( T \to 0 \) limit. The similarity of this last line with Sorbello’s \( Z_4 \), Eq. (27), is striking. The factor of 2 reflects whether the electron spin degeneracy has been accounted for explicitly or not. In fact, if in the last line of Eq. (33) the states \( q \) and \( q' \) are replaced by the unperturbed ones \( k \) and \( k' \), it reduces to Sorbello’s expression. This implies an intriguing equality indeed, and it shows that the two descriptions are closely related.

VI. THE CORRECTION TERM IN TERMS OF PHASE SHIFTS

For the evaluation of the correction term \( Z_{\text{corr}} \) as it is defined in Eq. (24) one needs the states \( | q > \). These states are the eigenstates of a system with one impurity in free space. It is known that the scattering states \( | \psi_k > \) for this system, which have a one-to-one correspondence to the free space states \( | k > \), are exact solutions of the Schrödinger for one impurity in free space as well. It appears that the evaluation of \( Z_{\text{corr}} \) becomes relatively simple if one uses the scattering states instead of the true eigenstates. We return to this point below.

The expansion of the scattering state \( < r | \psi_k > \equiv \psi_k(r) \) in terms of spherical harmonics is given by

\[
\psi_k(r) = \frac{4\pi}{\sqrt{\Omega}} \sum_L \ell^\prime Y_{L}^\ast(\hat{k}) R_\ell(r,k) Y_L(\hat{r}). \tag{34}
\]

The angular momentum label \( L \) combines the labels \( \ell \) and \( m \), so \( L = \ell m \), and \( R_\ell(r,k) \) is the radial solution of the Schrödinger equation at the energy \( \epsilon_k \) for a spherically symmetric potential \( v \) centered at the origin. For \( r \) outside the range of the potential \( R_\ell(r,k) \) can be written in terms of the scattering \( t \) matrix \( t_\ell = -\frac{1}{2} \sin \delta_\ell \exp(i\delta_\ell) \) as \( j_\ell(kr) - ik\ell h_\ell^\ast(kr) \), where \( \delta_\ell \) are the phase shifts. This means that for a plane wave \( R_\ell(r,k) \to j_\ell(kr) \). The box normalization in the system volume \( \Omega \) induces a discrete set of \( k \) values. In the properties to be presented below a delta function normalization will be used, which means that in Eq. (34) the system volume \( \Omega \) has to be replaced by \( 4\pi \). Using the expansion Eq. (34), the equality \( < k' | v | q' > = t_{k'k} \) which holds for scattering states \( | q > \to | \psi_k > \), and the overlap property for scattering states

\[
< k' | \psi_k > = \frac{\delta(k-k')}{k^2} \sum_L Y_L(k')Y_L^\ast(k) \left( 1 - i k\ell \right), \tag{35}
\]

one finds for \( Z_{\text{corr}} \)

\[
Z_{\text{corr}} = -\frac{4}{3\pi m} \int_0^\infty k^3 dk \left( \frac{\partial}{\partial \epsilon_k} \delta(\epsilon_k - \epsilon_F) \right) F(\epsilon_k) = \frac{2}{\pi} \left( F(\epsilon_F) + \frac{2}{3} \frac{\epsilon_F^2}{\epsilon_F^2 - \epsilon_F^4} \frac{\partial}{\partial \epsilon_F} \bar{F}(\epsilon_F) \right), \tag{36}
\]

in which the function \( F(\epsilon_k) \) is given by

\[
F(\epsilon_k) = \frac{1}{4} \sum_\ell (\ell + 1) \left( \sin 2\delta_\ell + \sin 2\delta_{\ell+1} \right) \left( \cos^2(\delta_\ell - \delta_{\ell+1}) + 1 \right), \tag{37}
\]

and \( \bar{F}(\epsilon_k) \equiv \frac{1}{4} F(\epsilon_k) \). Crucial steps of the derivation of Eq. (36) are given in Appendix A. This expression can be evaluated simply, because it is just a function of the phase shifts of the impurity potential at the Fermi energy.
$Z_{\text{corr}}$ as it is given by Eq. (30) has to be compared with the lowest order expression, obtained by the replacements $|q\rangle \rightarrow |k\rangle$ and $|q'\rangle \rightarrow |k'\rangle$. For the sake of a proper comparison this expression has to be evaluated in a similar way, by the use of scattering states. This way one obtains

$$Z_{\text{corr}}^0 = -\frac{4}{3\pi m} \int_0^\infty k^3 dk \left( \frac{\partial}{\partial \epsilon_k} (\delta(\epsilon_k - \epsilon_F)) \right) F^0(\epsilon_k) = \frac{2}{\pi} \left( F^0(\epsilon_F) + \frac{2}{3} F^0(\epsilon_F) \right),$$

in which the function $F^0(\epsilon_k)$ is given by

$$F^0(\epsilon_k) = \frac{1}{2} \sum_\ell (2\ell + 1) \sin 2\delta_\ell = \sum_\ell (2\ell + 1) \sin \delta_\ell \cos \delta_\ell, \quad (39)$$

and $F^0(\epsilon_k) \equiv \frac{1}{4} F^0(\epsilon_k)$. The right-hand sides of Eqs. (38) and (40) can have different numerical values, because the two elaborations are different in character. Comparison of these numerical values can be considered as a test of the error made in using scattering states instead of the true eigenstates. Another test of this error is obtained by evaluating the simplified lowest order result for $Z_{\text{corr}}$ explicitly, to be denoted as $Z_{\text{corr}}^{00}$, using the expansion (16). One finds

$$Z_{\text{corr}}^{00} = \text{tr} \{ n(h) - n(h_0) \} = \frac{2}{\pi} \sum_\ell (2\ell + 1) \sin \delta_\ell \cos \delta_\ell = \frac{2}{\pi} \frac{F^0(\epsilon_k)}{} \neq \frac{2}{\pi} \sum_\ell (2\ell + 1) \delta_\ell = Z_F, \quad (40)$$

in which $Z_F$ stands for the Friedel sum. The inequality in Eq. (41) must be attributed to the use of scattering states instead of the true eigenstates. The difference between these two types of states has been stressed by Fenton [21] and commented on by the present authors [22]. A scattering state is prepared such that it is an unperturbed state at some position in the system. An eigenstate has to be constructed using the boundary conditions of the system in addition to the properties of the potential. In terms of scattering theory eigenstates contain the influence of backscattering by the boundaries in addition to the information about the scattering by the potential. It is clear that the third member of Eq. (40) reduces to $Z_F$ in the small phase-shifts limit $\delta_\ell \to 0$.

Sorbello’s equation for $Z_d$, Eq. (27), can be evaluated through the use of scattering states as well. We first give the form corresponding to the eigenstates of $h$, denoted as usual by $|q\rangle$, followed by the result obtained by using scattering states.

$$Z_d = \sum_\ell \int_0^{r_0} r^2 dr \sum_q (2\ell + 1) \left( R^2 \langle r, k' \rangle - j^2 \langle k' r \rangle \right) = 4\epsilon_F \sum_\ell (2\ell + 1) \frac{\partial \delta_\ell}{\partial \epsilon_k} + 4k_F v_0^3 \epsilon_F \pi, \quad (41)$$

As above, for scattering states the potential matrix element becomes equal to the $t$ matrix element $t_{k'k}$. The energies $\epsilon_k$ and $\epsilon_q$ are equal, being connected by a delta function as shown in Eq. (35). Interestingly, this rewritten $Z_d$ is equal to our $Z_{\text{corr}}^{00}$ given by Eq. (38). This again shows the close relationship between the results obtained through the simplified approach presented here and Sorbello’s results.

Sorbello calculated $Z_d$ of Eq. (27) using the square well potentials described in [33]. To that end he derives his rewritten form Eq. (17), which we reproduce in a slightly different notation as

$$Z_d = \frac{4v_0 k_F}{3\pi} \int_0^{r_0} r^2 dr \sum_\ell (2\ell + 1) \left( R^2 \langle r, k' \rangle - j^2 \langle k' r \rangle \right) + \frac{4\epsilon_F}{\pi} \sum_\ell (2\ell + 1) \frac{\partial \delta_\ell}{\partial \epsilon_k} + 4k_F v_0^3 \frac{3\epsilon_F}{\pi}. \quad (42)$$

In the derivation has been used, that $\frac{2}{\pi^2} = h - v = h - \epsilon_F + \epsilon_F - v$, $G - G^0 = GvG^0$, $(h - \epsilon_F)G = -1$, $-\text{Im} Tr \{ G - G^0 \} = \sum_k (2\ell + 1) \frac{\partial \delta_\ell}{\partial \epsilon_k}$, and $\text{Im} G^0 \langle r, r \rangle = -k_F \sum_L j^2 \langle r \rangle$, and $\text{Im} G^0 \langle r, r \rangle = -k_F \sum_L R^2 \langle r \rangle$, with $R_L \langle r \rangle \equiv R(r, k_F) Y_L (\hat{r})$. For $r \leq r_0$ the radial solution $R(r, k_F) \propto j_L (k_F r)$, with $k_F = \sqrt{\epsilon_F + v_0}$. For reasons of a proper comparison we evaluated $Z_d$ according to Eq. (42) up to $\ell = 2$, because Sorbello restricted himself to $\ell_{\text{max}} = 0$. 


VII. NUMERICAL RESULTS

The expressions obtained will be evaluated for the same square well model potentials as were used in §III, in that employing a slight generalization of the potentials used by Sorbello. Results for $Z_d/Z_F$ and $Z_{corr}/Z^0_{corr}$ are shown in FIG. 3. Because the Friedel sum for the model square well potentials is rarely equal to unity, the use of ratios gives the proper measure for the screening, in which we follow Sorbello.

It is seen that for the stronger potentials, with $r_0 = 2/\lambda$, Sorbello’s boldly dashed curve lies somewhat lower than the dashed curve for the present description, while they display almost equal results for the higher $k_F$ values. The curves for the weaker potentials lie lower than those for $r_0 = 2/\lambda$. Although they differ considerably for smaller $k_F$ values, the curves approach each other for higher $k_F$. Both results imply a decrease of the inaccuracy related to the $|q| \to |\psi_k|$ replacement in the present description for states with increasing $k$ values. This is reasonable, because larger $k$ values correspond to smaller wave lengths, which probe the scattering potential more precisely, while the boundary effect decreases. As a guide for the eye the average for the two well widths are drawn as dotted lines. From the present description one comes to a direct valency of $0.85 \pm 0.15$ on the average, while this is $0.91 \pm 0.10$ for Sorbello’s description. So it appears that the $|q| \to |\psi_k|$ replacement is not too crude in determining a measure for the amount of screening. The screening mentioned by Sorbello is based mainly on the $r_0 = 1/\lambda$ potentials, because for these potentials his restriction to $\ell_{max} = 0$ is reasonable. If we correct for the higher $\ell$ values we find 0.82 for $Z_d/Z_F$ in aluminum instead of his 0.75. He used the latter value in mentioning a screening of 25%. For the sake of completeness we remark, that if one would compare the boldly dashed curve with the values given in Sorbello’s Table II one would observe considerable differences. This is due to the fact that for the $r_0 = 2/\lambda$ potentials the $\ell = 1$ and 2 terms contribute significantly. Taking everything together the available models and descriptions end up at a screening between 5 and 30%. Comparing with the largely metallic-density dependent result of Ishida, covering the entire range of no screening to complete screening, the present result can be considered as rather conclusive, in that complete screening is excluded.

In order to get some more insight in the $k_F$ dependences shown in FIG. 3 we display the quantities $Z^0_{corr}$, $Z_i$(pot) and $Z_F$ in FIG. 4. It is seen that all curves have a positive slope, apart from the one for $Z_F$ for the weaker $r_0 = 1/\lambda$ potential. This is certainly related to the seemingly deviant $Z_d/Z_F$ curve in FIG. 3 and the fact that the $Z_d/Z_F$ curves have been obtained by an accurate numerical evaluation of Eq. (12), while the $Z_{corr}/Z^0_{corr}$ results ‘suffer’ from the $|q| \to |\psi_k|$ replacement. The effect of this replacement is larger for the weaker potential, which can be seen from both $Z_{corr}/Z^0_{corr}$ curves in FIG. 3 and the $Z^0_{corr}$ curves in FIG. 4. This is understandable if one realizes, that the effect of the potential on the wave functions increases with its strength, while the effect of the boundaries remains unchanged. Further we observe that $Z^0_{corr}$, $Z_i$(pot) and $Z_F$ lead to different curves. The difference between $Z^0_{corr}$ and
Z_i(pot) as shown in FIG. 4 is certainly due to the $|q \rightarrow |\psi_{k}|$ replacement. However, Eq. (30) implies that for the screened Coulomb potential one should find $Z_i(pot) = Z_{0 \text{corr}} = Z_i = Z_F = 1$. This means that a difference between $Z_i(pot)$ and $Z_F$ uncovers some limitation of the use of the model square well potential. Although the differences in shape of the three potentials are known, in FIG. 5 we show their shapes for a certain $k_F$ value, for which we chose a value in the middle of 0.7.

FIG. 4: $Z_{0 \text{corr}}, Z_i(pot)$ and $Z_F$ plotted as a function of $k_F$, for the two square well potentials.

FIG. 5: $v(r)$ for the three potentials plotted as a function of $r$. 


VIII. THE FORCE EXPRESSION OF Bosvieux AND FRIEDEL

The starting expression of Bosvieux and Friedel for the driving force is

\[ F_{T=0} = - \langle \Psi | \nabla_{\mathbf{R}_1} (V_{ei} + \delta V) | \Psi \rangle, \]

in which the state \( |\Psi\rangle \) is a solution of the Schrödinger equation for the system in the presence of an applied field. This means that one has to solve the time dependent Schrödinger equation

\[ i \frac{\partial \Psi(t)}{\partial t} = \mathcal{H}(t) \Psi(t) \equiv (H + \delta V(t)) \Psi(t). \]

The subscript \( T = 0 \) is added by the present author in order to distinguish this force from the force given in Eq. (2). The derivation of Eq. (2), in which a solution of the Liouville equation is used, has been given in the literature many times. Because the approach through the system wave function is typical for the theory of Bosvieux and Friedel, and because some questions can be raised about their solution, we give crucial steps of the derivation. We solve Eq. (44) by using the interaction representation for \( \Psi(t) \), defined as

\[ \Psi_I(t) \equiv e^{iHt} \Psi(t). \]

The equation for \( \Psi_I(t) \) becomes

\[ i \frac{\partial \Psi_I(t)}{\partial t} = e^{iHt} \delta V(t) e^{-iHt} \Psi_I(t). \]

After integrating this equation and using that for \( t \rightarrow -\infty \) the system is in the ground state of the unperturbed system Hamiltonian \( H \), one finds for \( \Psi(t) \) linearly in \( \delta V \)

\[ \Psi(t) = -ie^{-iHt} \int_{-\infty}^{t} dt' e^{iHt'} \delta V(t') e^{-iHt'} \Psi_I(-\infty) + e^{-iHt} \Psi_I(-\infty). \]

With \( \delta V(t) = \delta V e^{at} \), applying the substitution \( t \rightarrow t' \equiv s \), and considering an arbitrary time in the present, so \( t = 0 \), this becomes

\[ \Psi(0) \equiv \Psi = -i \int_{0}^{\infty} dt e^{-(iH+\alpha)t} \delta V e^{iHt} \Psi_I(-\infty) + \Psi_I(-\infty). \]

If one calculates matrix elements with this \( |\Psi\rangle \), the factor \( e^{-iE_0 \infty} \) in the state \( |\Psi_I(-\infty)\rangle \) drops out so that just the ground state \( |\psi_0\rangle \) of \( H \) remains.

By this one finds for Eq. (48)

\[ F_{T=0} = - \langle \psi_0 | \nabla_{\mathbf{R}_1} (\delta V) | \psi_0 \rangle + i \int_{0}^{\infty} dt e^{-at} < \psi_0 | (\nabla_{\mathbf{R}_1} V_{ei}) e^{-iHt} \delta V e^{iHt} | \psi_0 > + c.c. \]

\[ = Z_i e \mathbf{E} + i \int_{0}^{\infty} dt e^{-at} < \psi_0 | \left[ \nabla_{\mathbf{R}_1} V_{ei}, e^{-iHt} \delta V e^{iHt} \right] | \psi_0 >. \]

Because \( H \) commutes with the coordinates \( \mathbf{R}_\alpha \) in \( \delta V \) only the electron coordinates survive. Using the definition of the force operator, Eq. (5), and the hermitian property of \( H \) it is clear that the time dependence can be applied to \( F_{op} \) as well, and Eq. (49) can be written as

\[ F_{T=0} = Z_i e \mathbf{E} - i e \int_{0}^{\infty} dt e^{-at} < \psi_0 | \left[ F_{op}(t), \mathbf{E} \cdot \sum_j \mathbf{r}_j \right] | \psi_0 >. \]

Interestingly, Eq. (50) is precisely the zero-temperature equivalent of Eq. (2). This becomes even more clear if one writes down the form which shows up after the reduction of Eq. (50) to single particle states denoted by \(|q>\).

\[ F_{T=0} = Z_i e \mathbf{E} - i e \int_{0}^{\infty} dt e^{-at} \sum_q <q | \left[ f^I(t), \mathbf{E} \cdot \mathbf{r} \right] |q >. \]
The force operator $f^1$ is defined in Eq. [3]. At $T = 0$ the sum over the single particle states has a sharp cut-off at $\epsilon_q = \epsilon_F$. The finite temperature equivalent of Eq. [51] can be written as

$$F = Z_i eE - i e \int_0^\infty dt \, e^{-\alpha t} \text{tr} \left\{ n(h) \left[ f^1(t), E \cdot r \right] \right\}, \quad (52)$$

in which the Fermi-Dirac distribution $n(\epsilon)$ has been inserted, see Eq. [13]. Clearly, Eq. [52] is completely equivalent to Eq. [12] of the present text. By this electromigration theory can be considered as being unified. Apparently, the starting formula of Bosvieux and Friedel was correct, but these authors did not recognize its precise contents. In fact, they wrote down surface-integral terms, by this not appreciating the hermitian property of the system Hamiltonian. This property implies that these terms are zero, but their full-screening results were derived from these terms. In addition, they missed the power of their starting formula, Eq. [153], by taking the $a \to 0$ limit in too early a stage of the derivation.

IX. CONCLUDING REMARKS AND PERSPECTIVES

The amount of screening of the direct force on a proton in an electric-current carrying metal has been shown to lie between 5 and 25%. By this the full-screening prediction of Bosvieux and Friedel has been invalidated, completely in agreement with an earlier result obtained by Sorbello.\textsuperscript{24} On top of that, the surface integral terms used by Bosvieux and Friedel to derive their full-screening result appear to be zero, due to the hermitian property of the Hamiltonian. Interestingly, it has been shown explicitly that the starting expression of Bosvieux and Friedel for the driving force is the zero-temperature limit of all linear-response expressions used in the literature since their introduction by Kumar and Sorbello.\textsuperscript{2,3}

All calculations up to now use a jellium model for a metal, or are not applicable to transition metals.\textsuperscript{15} In view of the description presented it becomes feasible to account for real metallic effects. These effects have been accounted for for the wind force to a large detail, but for the direct force this was too much involved up to now. Such a development would be interesting, because this may lead to an explanation of a measured result which has not been understood yet, up to now. For most hydrides a direct valency for the hydrogen has been measured which is of the order of unity. However, in Nb(H) a direct valency was found of about 0.44. Such a deviating value may arise from multiple scattering effects of the electrons around a proton surrounded by metallic atoms, which can be accounted for in a finite-cluster description. It is worth while to investigate this possibility, because in the development of the description of the wind force surprising positive values for the wind valence in V(H) and Nb(H) were found, which were in agreement with experiment.\textsuperscript{12} The surprise comes from the fact, that in a system composed of a finite cluster embedded in a jellium the electron dispersion relation is still free-electron like, from which one would expect a negative wind valence. The calculated result must be due to the rather strong multiple scattering effects, which were accounted for explicitly. Similarly, it is worth while to develop a finite cluster description for the direct valency, which is a straight generalisation of the impurity in a jellium description implemented so far. This is a feasible development if one uses the simplified treatment presented above, of which it has been shown that the expressions can be evaluated in terms of the scattering phase shifts of the constituent atoms. A slightly more explicit hint can be found elsewhere.\textsuperscript{24}

Acknowledgement I want to thank Jacques Friedel for an interesting conversation and an extended correspondence over the recent months.

APPENDIX A: CRUCIAL STEPS IN THE DERIVATION OF EQ. [30]

For the evaluation of $Z_{corr}$ defined in Eq. [26] one needs the momentum matrix element $p_{q'q}$ and the matrix element of the commutator with the statistical distributions. For $p_{q'q}$ one writes

$$p_{q'q} = \frac{(4\pi)^2}{8\pi^3} \sum_{LL'} i^{L-L'} Y_{L'}(\hat{k}') Y_L^* (\hat{k}) \int d^3 r R_{L'}^* (r) p R_L (r),$$

(A1)

in which Eq. [51] with $\Omega \to 8\pi^3$ has been used for the wave functions and $R_L (r) \equiv R_L (r, k) Y_L (\hat{r})$. If one represents the scattering potential by a square well with depth $v_0$ the inner radial solution is a Bessel function as well, so $R_\ell (r, k) = A_{\ell} j_\ell (k_v r)$, with $k_v = \sqrt{k^2 + v_0}$, and one finds

$$\int Y_{L'}^* (\hat{r}) p R_L (r) d\hat{r} = i^{L-L'} k_v D_{L' L} R_{\ell' \ell}(r, k),$$

(A2)
in which the equality
\[ \int Y_L^* (\hat{r}) \mathbf{p} j_L(r) d\hat{r} = i^\ell - k \mathbf{D}_{\ell' \ell} j_{\ell'}(kr) \]  \hspace{1cm} (A3)

has been used and
\[ \mathbf{D}_{\ell' \ell} = \int dk Y_L^* (\hat{k}) \hat{k} Y_L(\hat{k}). \]  \hspace{1cm} (A4)

The double \( \ell \)-label in Eq. (A2) refers to the fact, that the factor \( A_\ell \) is not changed by the momentum operation and the angular integration, so that
\[ k_\nu R_{\ell' \ell}(r, k) = k_\nu A_{\ell' \ell} R_{\ell' \ell}(r, k) \rightarrow k (j_{\ell'}(kr) - i k t_\ell h_{\ell'}^* (kr)). \]  \hspace{1cm} (A5)

If one substitutes Eq. (A2) in Eq. (A1) one obtains
\[ p_{qq'} = \frac{2}{\pi} \sum_{LL'} Y_{LL'}(\hat{k'}) Y_{LL'}^*(\hat{k}) \mathbf{D}_{LL'} I^{RR}_{\ell' \ell}(k', k) \]  \hspace{1cm} (A6)

with
\[ I^{RR}_{\ell' \ell}(k', k) = \int_0^\infty r^2 dr k_\nu R_{\ell' \ell}(r, k') R_{\ell' \ell}(r, k), \]  \hspace{1cm} (A7)

and in which \( k_\nu = k_\nu \) inside the range of the potential and \( k_\nu = k = k_\nu \) outside of it. Using the equality
\[ \int_0^\infty r^2 dr j_\ell(k') j_\ell(kr) = \frac{\pi \delta(k - k')}{2k^2}, \]  \hspace{1cm} (A8)

it appears to be possible to reduce the integral \( I^{RR}_{\ell' \ell}(k', k) \) to
\[ I^{RR}_{\ell' \ell}(k', k) = \frac{k \pi \delta(k - k')}{2} \overline{I^{RR}}_{\ell' \ell}, \]  \hspace{1cm} (A9)

in which
\[ \overline{I^{RR}}_{\ell' \ell} = 1 - i k t_\ell + i k t_\ell^* - 2 i k t_\ell i k t_\ell^*. \]  \hspace{1cm} (A10)

Now we turn to the other matrix element in Eq. (26). Using Eq. (16) one finds
\[ < q' | r, n(h) - n(h_0) | q' > = - \int_0^\beta ds < q' | r, n(h) e^{sh} v e^{-sh_0} (1 - n(h_0)) | q' >. \]  \hspace{1cm} (A11)

We remind the reader that in this equation \( h \) and \( v \) just refer to the system with one impurity, so to \( h^1 \) and \( v^1 \). Now we use the equality (20) and the following related equality
\[ [e^{\beta h}, r] = - i \frac{m}{h} \int_0^\beta ds \mathbf{p}(s) e^{\beta h} \]  \hspace{1cm} (A12)

twice, one time for \( h \) and one time for \( h_0 \). By that the commutator in the right hand side of Eq. (A11) can be written as
\[ [r, n(h) e^{sh} v e^{-sh_0} (1 - n(h_0))] = - \frac{i}{m} n(h) \left( \int_0^\beta ds \mathbf{p}(s') (1 - n(h)) e^{sh} v e^{-sh_0} \right) \]
\[ - \int_0^\beta ds' \mathbf{p}(s') e^{sh} v e^{-sh_0} + e^{sh} v e^{-sh_0} \mathbf{p} \left( s - \beta n(h_0) \right) \left( 1 - n(h_0) \right). \]  \hspace{1cm} (A13)

It will be clear that \( \mathbf{p}(s) \) in the first and second term refers to \( h \).

Now we develop the \( qq' \) matrix element of this operator as it occurs in Eq. (A11). In that we will make use of the property proven above through Eq. (A12) with (A3), namely that the energies \( \epsilon_q \) and \( \epsilon_{q'} \) in the matrix element \( p_{qq'} \)
are equal, and of the equality of the energies $\epsilon_k$ and $\epsilon_q$ in the overlap $<k|q>$, see Eq. (A3). In the first and second term we have to insert two complete sets, one $q$ set $|q''><q'''|$ and one $k$ set $|k''><k'''|$. In the third and fourth term one needs the complete $k$ set only. This way one writes for the $qq'$ matrix element in the left hand side of Eq. (A11)

$$<q|\{r, n(h) - n(h_0)\}|q'> = \frac{i\beta^2}{m} n_q \left[ \sum_{q''} \sum_{k''} p_{qq''} \left( \frac{1}{2} - n_{q''} \right) t_{k''q''} + \sum_{k''} t_{k''q''} k'' \left( \frac{1}{2} - n_{k''} \right) \right] (1 - n_{k''}) <k''|q'> \tag{A14}$$

in which the potential matrix element $v_{qk'} = v_{k'q}$, between an exact scattered state $|q'> = |\psi_k> \tag{A4}$, and an unperturbed state, a plane wave $|k'> \tag{A5}$, has been replaced by the corresponding $t$ matrix element $t_{k'q}$.

By now we have developed the means for bringing $Z_{corr}$ in a manageable form. One has to take the inner product of the matrix element given by Eq. (A14) with $4 p_{q'q''}$ and to carry out the summations. Because the summations are equivalent to integrals and the absolute values of all $k$-vectors involved are equal through delta functions, one just has to carry out the angular integrations. We write for $Z_{corr}$ in Eq. (A9)

$$Z_{corr} = \frac{i}{3} \int dk \int dk' \int dk'' \left( \int dk_{3m} \right) <q|\{r, n(h^1) - n(h_0)\}|q'> p_{q'q}, \tag{A15}$$

in which the right hand side of Eq. (A14) is supposed to have been substituted. The angular integration over $k_{3m}$ applies to the first term in the right hand side of Eq. (A14) only. The product of statistical factors which shows up can be simplified and in the $T \to 0$ limit be written as follows

$$-\beta^2 n_k(1 - n_k) \left( \frac{1}{2} - n_k \right) = \frac{1}{2} \frac{\partial}{\partial \epsilon_k} (n_k(1 - n_k)) \rightarrow \frac{1}{2} \frac{\partial}{\partial \epsilon_k} \delta(\epsilon_k - \epsilon_F). \tag{A16}$$

If one substitutes this equality, uses Eq. (A8) with Eqs. (A9) and (A10), and Eq. (A14), accounts for the factor of 2 due to the spin degeneracy and carries out all angular integrations, one finds for $Z_{corr}$ of Eq. (A10)

$$Z_{corr} = \frac{2}{3\pi m} \int_0^\infty k^2 dk \frac{\partial}{\partial \epsilon_k} \delta(\epsilon_k - \epsilon_F) \sum_{LL'} D_{LL'} \cdot D_{L'L} \cdot (1 - i \epsilon \ell \ell') \times \left( t_{\ell'}^R \ell_{\ell'}^R + t_{\ell}^R \ell_{\ell}^R \right) k^2 \ell_{\ell'}^R \ell_{\ell}^R = -\frac{4}{3\pi m} \int_0^\infty k^2 dk \left( \frac{\partial}{\partial \epsilon_k} \delta(\epsilon_k - \epsilon_F) \right) F(\epsilon_k), \tag{A17}$$

in which has been used that

$$\ell_{\ell'}^R = \cos(\delta_\ell - \delta_\ell') e^{-i(\delta_\ell - \delta_\ell')}, \tag{A18}$$

and that

$$\sum_{mm'} D_{LL'}^m D_{L'L}^{m'} = \frac{1}{3} \delta_{mm'} \left( (\ell + 1) \delta_{\ell',\ell+1} + \ell \delta_{\ell',\ell-1} \right). \tag{A19}$$

In the right hand side of Eq. (A17) one recognizes the second member of Eq. (A5), by which the derivation has been completed. The derivations leading to Eqs. (38), (40) and (41) are similar, and they are simpler as well.

---

1. L.J. Sham, Phys. Rev. B 12 (1975) 3142.
2. C. Bosvieux and J. Friedel, J. Phys. Chem. Solids 23 (1962) 123.
3. R. S. Sorbello, Phys. Rev. B 31 (1985) 798.
4. For a review, see J. van Ek and A. Lodder, Defect and Diff. Forum 115-116 (1994) 1.
5. J.P. Dekker, A. Lodder and J. van Ek, Phys. Rev. B 56 (1997) 12167.
6. J.P. Dekker and A. Lodder, Phys. Rev. B 57 (1998) 6687.
7. J.P. Dekker and A. Lodder, J. Phys.: Cond. Matter 10 (1998) 1598.
8. For a review, see R. S. Sorbello, in Solid State Physics, Vol. 51, Eds. H. Ehrenreich and F. Spaepen (Academic Press, San Diego, 1997) 159.
9. P. Kumar and R.S. Sorbello, Thin Solid Films 25 (1975) 25.
10. A.H. Verbruggen and R. Griessen, Phys. Rev. B 32 (1985) 1426.
11. L. Turban, P. Nozières and M. Geri, Journal de Physique 37 (1976) 159.
12. A. Lodder, Solid State Commun. 71 (1990) 259.
13. A. Lodder, J. Phys.: Cond. Matter 3 (1991) 399.
14. A. Lodder, Solid State Commun. 79 (1991) 143.
15. H. Ishida, Phys. Rev. B 51 (1995) 10345.
16. P.R. Rimbey and R.S. Sorbello, Phys. Rev. B 21 (1980) 2150.
17. A. Lodder, J. Phys. Chem. Solids 51 (1990) 19.
18. A. Lodder, Physica A158 (1989) 723.
19. J.M. Ziman, Principles of the Theory of Solids, Cambridge Univ. press, 1992, Ch. 5.
20. R.S. Sorbello, Solid State Commun. 76 (1990) 747.
21. E.W. Fenton, Solid State Comm. 22 (1977) 63.
22. A. Lodder, Physica 97B (1979) 156.
23. A. Lodder and M.G.E. Brand, J. Phys. F: Met. Phys. 14 (1984) 2955.
24. A. Lodder, Defect and Diff. Forum 237-240 (2005) 695.