Electromigration Force on a Proton with a Bound State

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\textbf{Keywords:} Bound State, Electric Wind, Electromigration, Proton

\textbf{Abstract}

The driving force on an ion in a metal due to an applied electric field, called the electromigration force, is built up out of two contributions, a wind force and a direct force. The wind force is due to the scattering of the current carrying electrons off the ion. The direct force works on the effective charge of the ion. In the present work we concentrate on the direct force on a migrating proton embedded in an electron gas. For this force a sign change is obtained as soon as a bound state is formed. In recent calculations hardly a sign change was seen, although a bound state was found in a self-consistent-potential for lower electron densities. Here we show that a supplementary term shows up, as soon as one accounts for the bound state explicitly. By this the problem has been solved regarding a possible lack of completeness of the published formalism. The results presented are based on square-well model potentials. By using different depths it is possible to show results for potentials without a bound state and accommodating one bound state.

\textbf{Introduction}

In an electric field $E$ applied to a metal or semiconductor the phenomenon of electromigration may occur [1]. The technological importance of this current-driven ion transport phenomenon is in its possible failure-influence, especially at miniaturization [2]. The driving force $F$ on the ion consists not only of the direct electrical force proportional to the effective direct valence $Z_{d}$, but also of an indirect force via the electrons carrying the current, proportional to the wind valence $Z_{w}$, so

$$F = (Z_{d} + Z_{w})eE$$

The complexity of electromigration comes from the fact that both electron transport and ionic transport have to be taken into account. Nevertheless, there is an agreement between theories of electromigration that the wind force $Z_{w}eE$ is described via the transport cross-section [1]. On the other hand, the magnitude of the direct valence has been the subject of a controversy for over forty years [3, 4, 5, 6, 7]. Friedel [3] and Nozières [5] defended a complete screening of the direct force, so $Z_{d} = 0$, in which vision only a wind force is operative. Others found a negligible screening [4] or a limited screening of at most 25% [6]. It was only recently that the sting was taken out of this controversy [7, 8, 9]. It was shown that the controversial results were incomplete and, after repairing that, electromigration theory became a unified theory [10].

The screening electron of the migrating ion, let us concentrate on a proton, has always been treated as a free electron, which is exchangeable with other electrons in the electron sea [6, 7]. This is correct for most of the metallic hydrides. However, in the interpretation of their recent experimental results for yttrium hydrides, Van der Molen \textit{et al}. considered the possibility of the formation of a bound state, such as $H^{+}$ ions [11]. For a singly and a doubly occupied bound state one would expect $Z_{d} = 0$ and $Z_{d} = -1$ respectively. Unfortunately, using an extension of the description of the electronic structure to conditions leading to a bound state, Vincent \textit{et al}. obtained $Z_{d}$ values which were not convincingly negative [12]. This has led to the conclusion that the published formalism might be not complete.
In the present study we want to repair that. We shall show that, by accounting for the bound state explicitly, an additional term is generated in the published expression for \( Z_d \). Interestingly, this term appears to be negative. By numerical calculations we show that this negative contribution leads to a considerable reduction of the calculated \( Z_d \). We use Rydberg atomic units, with \( \hbar = 1 \) and \( m_e = \frac{1}{2} \).

**Term in \( Z_d \) due to a bound state**

We start by giving two published expressions for \( Z_d \). Sorbello (S) finds, for \( Z_d \) [6]

\[
Z_d^S = -\frac{2}{3\pi m_e} \text{Im}\{\text{tr}\{p^2(G(\varepsilon_F) - G^0(\varepsilon_F))\}\}
\]  

(2)

where \( \text{tr} \) stands for the trace operation. The single particle Green’s function \( G(\varepsilon) \) for an impurity in a jellium and the free electron Green’s function \( G^0(\varepsilon) \) are given by

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

(3)

in which \( h = h_0 + \nu \), \( \nu \) is the impurity potential, and the \( a \to 0^+ \) notation is used. It is clear from Sorbello’s work that \( Z_d^S \) can be calculated exactly only for a square-well model potential. However, a more tractable form has recently been derived. This is done by first writing the trace operation in \( Z_d^S \) in terms of two sets of states as follows [7]

\[
Z_d^S = -\frac{2}{3\pi m_e} \text{Im}\sum_q \sum_{k'} <q|k'> k^2 G_{k'}^0(\varepsilon_F) <k'|\nu|q>G_{\nu}(\varepsilon_F)
\]

(4)
Figure 2: The Friedel sum $Z_F$, and $Z_d$ and $Z_d^q$ according to Eq. (8), for $V/V_c = 0.99$ and $V/V_c = 1.01$.

In the latter well, just one bound state has been formed.

in which $|q\rangle$ represents a complete set of eigenstates of $\hat{h}$ and $|k\rangle$ are free electron states. If one chooses the eigenstates to be represented by scattering states, so

$$\langle r|q\rangle \rightarrow \psi_k^+(r) = 4\pi \sum_{lm} A_l(k) R_l(k, r) Y_{lm}(\hat{r}),$$

(5)

in which $R_l(k, r)$ are exact solutions of the radial Schrödinger equation for the ionic potential $\upsilon(r)$ at $\epsilon_k = k^2$ scattering energy, and $A_l(k) = i^{l} e^{i\delta_l(k)}$, Eq. (4) reduces to [7, 12]

$$Z_d^q = \frac{2}{3} \frac{d}{d\epsilon_F} \int_0^{\epsilon_F} \frac{3}{2} \epsilon_k^2 d\epsilon_k \delta(\epsilon_F - \epsilon_k) \frac{F_s(k)}{k} = F_s(k_F) + \frac{k_F^2}{3} \frac{d}{dk_F} \left( \frac{1}{F_s(k_F)} \right)$$

(6)

This is simply a function of the one-electron scattering phase shifts $\delta_l(k)$ at the Fermi momentum $k_F$, because the $F_s$ function has the form

$$F_s(k) = \frac{1}{\pi} \sum_{\ell=0}^{\infty} (2\ell+1) \sin 2\delta_l(k)$$

(7)

by which $Z_d^q$ can be calculated for any scattering potential. By the way, note that for small $\delta_l$ the function $F_s$ takes the form of the Friedel sum $Z_F$. Although this evaluation is exact, it is an assumption that the use of scattering states is allowed. For a discussion of this point we refer to earlier work [7].

If a bound state is formed, the evaluation (4), using the states $|q\rangle$ given by Eq. (5), is no longer complete. One has to add the bound state, to be denoted as $|b\rangle$. If one adds, to the expression given
by Eq. (4), a term in which the states $|q>$ have been replaced by the bound state $|b>$ one obtains

$$Z_d = Z_d^q + Z_d^b$$

in which

$$Z_d^b = -\frac{2}{3\pi m_e} \text{Im} \sum_k <b|k^2 G_k^0(\varepsilon_F) <k|\psi>|b> G_b(\varepsilon_F)$$

$$= \frac{8}{3} \int d^3 k <b|k^2 \delta(\varepsilon_F - \varepsilon_k) \frac{\psi_k}{\varepsilon_F - \varepsilon_b} >$$

$$= \frac{16\pi}{3} \int_0^\infty \frac{3}{2} \varepsilon_k^2 d\varepsilon_k \delta(\varepsilon_F - \varepsilon_k) \frac{<b|\psi_k >}{\varepsilon_F - \varepsilon_b} = \frac{16\pi}{3} \frac{3}{\varepsilon_F - \varepsilon_b} <b|k^2 \delta(\varepsilon_F - \varepsilon_k) \frac{\psi_k}{\varepsilon_F - \varepsilon_b} >$$

The imaginary part of $G_b(\varepsilon_F)$ does not contribute, because $\varepsilon_F - \varepsilon_b \neq 0$, by which Im$G_k^0(\varepsilon_F)$ reduces to $-\pi\delta(\varepsilon_F - \varepsilon_k)$. Numerical values for $Z_d^b$ are easily obtained after evaluation of the overlap integral

$$<b|k> = \frac{1}{\sqrt{8\pi r^3}} \int d^3 r \psi_b(r) e^{ikr} = \frac{4\pi}{\sqrt{8\pi r^3}} \int_0^\infty r^2 dr \psi_b(r) j_0(kr)$$

and the potential matrix element

$$\psi_{bk} = \frac{1}{\sqrt{8\pi r^3}} \int d^3 r \psi_b(r) \psi(r) e^{ikr} = \frac{4\pi}{\sqrt{8\pi r^3}} \int_0^\infty r^2 dr \psi_b(r) \psi(r) j_0(kr)$$

in which $j_0$ stands for a spherical Bessel function. Because the lowest bound state is a simple $s$ state, being a real function, the complex-conjugation asterisk on $\psi_b$ has been omitted. Although we are not
going to make use of it in the numerical calculations, we mention the following equality [13]

\[ \nu_{bk} = \frac{1}{\sqrt{8\pi}} \int d^3r \psi_b(r)(h-h_0)e^{ikr} = \frac{1}{\sqrt{8\pi}} (\varepsilon_{bk}-\varepsilon_k) \langle b|k \rangle \]  

(12)

Figure 4: \( Z_d \) and the bound state energy, in fact -\( E_{\text{bound}} \), for the two well-depths \( V/V_c = 1.1 \) and 1.5. In addition, results are plotted for \( Z_d^q \) corresponding to a self-consistent potential, with one bound electron and two bound electrons for larger \( r_s \) values; see Vincent et al. [12].

Interestingly, one sees right away that \( Z_d^b < 0 \), if one substitutes this equality in Eq. (9).

The consequences will be illustrated by calculations using a model potential accommodating one bound state. This means that the results to be presented go beyond earlier work for potentials without a bound state [6, 7].

Results
We present results for the original expression \( Z_d^q \), see Eq. (2), for \( Z_d \) according to Eq. (8), and for \( Z_d^q \), see Eq. (6). Square-well model potentials have been used with width \( r_0 = 1/\lambda \), where \( \lambda = (4k_F/\pi)^{1/3} \), the inverse of the Thomas-Fermi screening length. In earlier work, the well-depth \( V \) has always been restricted by the condition \( V/V_c < 1 \), where \( V_c = \pi^2/8m_e r_0^2 \) is the critical value of the well depth for which a bound state forms [6, 7]. Now we shall focus on potentials with \( V/V_c > 1 \); accommodating one bound state.

In Fig. 1 the quantities \( Z_d \) and \( Z_d^q \) are shown for three well depths, all giving rise to one bound state. In another figure we shall show some bound-state energies. All quantities are plotted as a function of the density parameter \( r_s = (\sqrt[3]{\pi} n_0)^{1/3} \), \( n_0 \) being the electron density. So, small \( r_s \) values correspond to metallic behaviour with a high density. The \( r_s \) values for Al and Na are 2.07 and 3.93, respectively. It is seen that, while almost all \( Z_d^q \) values are positive, the \( Z_d \) curves lie much lower. The curves for the \( V/V_c \) values 1.4 and 1.7 are in the negative domain for almost all \( r_s \) values.

In order to see how strong the effects are, in Fig. 2 we show \( Z_d^q \) for a well with no bound state yet, and for one in which just one bound state has started to be formed, with \( V/V_c = 1.01 \). For the latter
case we show $Z_d$ as well, of course. In addition, the corresponding Friedel sum values have been plotted. The difference between the two $Z_d^q$ curves is very small, but the effect of the additional term giving rise to $Z_d$ is clearly visible; particularly for larger $r_s$ values.

Figure 5: Results for $\tau^{-1}_{\text{exact}}$, for square wells with $V/V_c = 0.99$ to 1.5.

In Fig. 3 the quantities $Z_d^S$ and $Z_d^q$ are shown for a well without a bound state and for one with $V/V_c = 1.5$. In addition, the corresponding Friedel sum values have been plotted. It is clear that the $Z_d^S$ values are not at all small, although an evaluation is used which is claimed to be exact for a square well [6]; which claim seems to be correct [7]. Another point is that the $Z_d^q$ curves are markedly distinguishable from the $Z_d^S$ curves. That point has been discussed earlier, and it is supposed to arise from the fact that, in deriving Eq. (6) from Eq. (2), scattering states have been used instead of true eigenstates [7]. For the sake of completeness, we mention that Sorbello considered the ratio $Z_d^S/Z_F$ to be a better measure, for the direct valence, than $Z_S$ itself. The reason is that square-well potentials lead to a certain value for the Friedel sum $Z_F$, which is not necessarily equal to unity. Both Sorbello and the present author gave values for the ratio only [6, 7]. Similarly, only the ratio $Z_d^q/Z_d^0$ was given before, with $Z_d^0 = -4\pi\sqrt{\mu_F}\nu_{kk}$ [7, 12]. For this reason it may be helpful to know that, for a screened Coulomb potential $-Ze^{2}\lambda/r$ the quantity $Z_d^0$ appears to be equal to the valence $Z_v$, which is equal to unity for a proton.

Fig. 4 shows $Z_d$ values for two well depths and the corresponding bound state energies. It is seen that for $V/V_c = 1.1$ the bound state lies just below the $E = 0$ line, while the bound state energy for $V/V_c = 1.5$ is already considerable. In addition $Z_d^0$ values are shown which are based on self-consistently calculated phase shifts for a paramagnetic host; which results are part of Ref.[12]. These potentials could be generated including the $Z_F = 1$ constraint. These results contributed to the conjecture that the published theory for $Z_d$ might be incomplete. Although for the potentials with a doubly bound state the $Z_d^q$ values become negative for larger $r_s$ values, for the potential with a neutral hydrogen the values are positive over the entire $r_s$ range.

We want to conclude this part by making a general remark. One sees that all valence curves have a negative slope. We think that this can be understood physically if one realizes that, for increasing $r_s$ and so for an increasing dilution of the electron gas, the proton will attract its
screening electron more and more strongly; even if it is not yet in a bound state. By that means, it may give rise to a larger screening force.

![Graph showing results for \(\tau^{-1}_{2\text{nd-order}}\) for square wells with \(V/V_c\) = 0.99 to 1.5.]

Figure 6: Results for \(\tau^{-1}_{2\text{nd-order}}\), for square wells with \(V/V_c = 0.99\) to 1.5.

One might wonder whether a difference is seen in scattering strength for potentials with and without a bound state. This leads us to the other contribution to the driving force, see Eq. (1), namely the wind force. The wind force is proportional to the inverse transport relaxation time \(\tau^{-1}\) of the migrating impurity [1]. Its exact value is given by

\[
\tau^{-1}_{\text{exact}} = n_{\text{imp}} \frac{8\pi}{k_F} \sum_l \left(\ell+1\right) \sin^2(\delta_{\ell+1}-\delta_l) \tag{13}
\]

which is a function of the impurity scattering phase shifts at the Fermi energy. Its value, to lowest order in the scattering potential, is

\[
\tau^{-1}_{2\text{nd-order}} = n_{\text{imp}} \pi k_F \sum_l \left(\ell+1\right) (\nu_l-\nu_{l+1})^2, \tag{14}
\]

where \(\nu_l = \int_0^\infty r^2 dr j_l^2(kr)v(r)\).

Results are shown in Figs. 5 to 7. Because only relative values are of interest, \(n_{\text{imp}}\) has been taken to be equal to the density of electrons \(n_0\). Neither Fig. 5 nor Fig. 6 show an appreciable increase in scattering strength in going from a potential with no bound state, with \(V/V_c = 0.99\), to one in which just one bound state has formed, with \(V/V_c = 1.01\). This might even be considered to be obvious, because the scattering strength depends upon properties only at the Fermi energy, which lies way above a bound-state energy. Comparing the two figures, one sees nicely that, for weaker potentials, \(\tau^{-1}_{\text{exact}} > \tau^{-1}_{2\text{nd-order}}\) while, for the stronger potential, the reverse holds. This property is shown more explicitly in Fig. 7. For a very weak potential, the two \(\tau^{-1}\) values are equal, for \(V/V_c = 0.99\) the exact value is larger while, for \(V/V_c = 1.4\), the value to lowest order in the potential has already increased.
Conclusions
The magnitude of the direct force, needed for the calculation of the driving force on an atom migrating under the influence of an applied electric field in a metal, see Eq. (1), is investigated for potentials which accommodate a bound state. In treatments published until now, the screening electron was effectively free, and the reduction of the bare valency of the proton was shown to be at most 25%. However, for a bound state one would expect a considerable reduction; even to negative values of $Z_d$. Using an improved description, in which the bound state was accounted for explicitly, we indeed find such a reduction. By this, the uncertainty regarding the completeness of the formalism developed in the literature has been resolved [12].

Figure 7: Results for $\tau^{-1}_{\text{exact}}$ and $\tau^{-1}_{\text{2nd-order}}$, for square wells with $V/V_c = 0.2$ to 1.4.

The presented results can also be seen as an independent justification of the consensus point of view regarding the controversy mentioned in the Introduction. It is only a bound electron that can cancel the direct force on the proton, and not just a screening electron, although this has been claimed for many years [3, 5, 10].

In view of recent experimental results [11], it may be interesting to apply the improved description to self-consistently generated potentials with a bound state.

Acknowledgement
The author wishes to acknowledge an interesting email exchange in December 2008 and a nice encounter in April 2009 with Prof. Philippe Nozières.

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