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Description of a migrating proton embedded in an electron gas

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Abstract
The direct force on a migrating proton embedded in an electron gas is calculated by implementing recently derived theoretical expressions for this quantity. A self-consistent Kohn–Sham calculation of the scattering potential leads to a doubly populated bound state and a sign change of the direct charge at lower electron densities. A self-consistent calculation under the constraint of single occupancy leads to positive values for all densities. This result is supported by employing constrained model potentials as well. A special constraint on the screening of a proton, related to the strength of the dipolar backflow pattern around it, results in a fairly constant value around unity for the direct charge in the whole metallic density range. Results based on square-well model potentials with prefixed width and depth show a lowering of the direct charge as soon as a bound state is formed. An open question remains regarding the completeness of the formalism in view of the fact that no cancellation of the direct charge is found for a system with a bound state.

1. 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 phenomenon is in its possible failure influence, especially in miniaturization [2]. The effective driving force (**F**) on the ion consists not only of the direct electrical force on the ion proportional to the direct charge Z_d, but also of an indirect force via the electrons carrying the current, proportional to the wind charge Z_w, so

$$\mathbf{F} = (Z_d + Z_w)\mathbf{E}. \tag{1}$$

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 $Z_w\mathbf{E}$ is described via the transport cross section [1]. On the other hand, the magnitude of the direct charge has been the subject of controversy for over 40 years [3–7]. Friedel [3] and Nozières [5] defended a complete screening of the direct force, so $Z_d = 0$, in which case 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 out of this controversy was removed [8, 9]. It was shown that the controversial results were incomplete, and after making a treacherously hidden trap explicitly, electromigration theory could be considered as being unified. However, until now the screening electron of the migrating impurity (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]. It would be interesting to extend the study to conditions leading to a possible bound state. For a singly and a doubly occupied bound state one would expect $Z_d = 0$ and -1, respectively. Such a result would be new compared to established predictions of a limited screening [6, 7]. In fact, this is the aim of the present study. Using two published expressions for Z_d and an expression for a related quantity, we want to make clear what is the present status of the theory. Sorbello (S) finds [6] for Z_d:

$$Z_d^S = -\frac{2}{3\pi m_e}\,\mathrm{Im\,Tr}\left\{p^2\left(G(\epsilon_F) - G^0(\epsilon_F)\right)\right\}, \tag{2}$$

where Tr stands for the trace operation. The single-particle Green's function $G(\epsilon)$ for an attractive screened static impurity in a jellium, with $h = h_0 + v$, and the free-electron Green's function $G^0(\epsilon)$ are given by, using the $a \to 0^+$ notation,

$$G(\epsilon) = \frac{1}{\epsilon + \mathrm{i}a - h} \qquad \text{and} \qquad G^0(\epsilon) = \frac{1}{\epsilon + \mathrm{i}a - h_0}$$
$$\text{with } h_0 = \frac{p^2}{2m_e}. \tag{3}$$

It is clear from Sorbello's work that $Z_{\mathrm{d}}^{\mathrm{S}}$ can be evaluated exactly for a square-well model potential only. We will return to this at the end of section 2 and in section 3. Fortunately, if one evaluates the trace operation in equation (2) in terms of single-particle scattering states belonging to the Hamiltonian h one finds [7] the following expression:

$$Z_{\mathrm{d}} = F_s(k_{\mathrm{F}}) + \frac{k_{\mathrm{F}}^2}{3}\frac{\mathrm{d}}{\mathrm{d}k_{\mathrm{F}}}\left(\frac{1}{k_{\mathrm{F}}}F_s(k_{\mathrm{F}})\right). \tag{4}$$

This is simply a function of the one-electron scattering phase shifts $\delta_\ell(k)$ at the Fermi momentum k_{F}, because the F_s function has the form

$$F_s(k) = \frac{1}{\pi}\sum_{\ell=0}^{\infty}(2\ell+1)\sin 2\delta_\ell(k). \tag{5}$$

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]. The limiting value k_{F} for occupied states is derived from a given density n_0 by the $k_{\mathrm{F}} = (3\pi^2 n_0)^{1/3}$ relation.

Till now only square-well model calculations were done [6, 7], and recently just a constructed potential was implemented [9]. We want to improve on that by using self-consistent potentials to proton screening. Interestingly, we find that in our self-consistent potential a bound state is formed for lower metallic densities. Such a bound state was avoided systematically [6, 7] earlier, although its possible nontrivial role in strong-coupling theory for the driving force in electromigration was pointed out explicitly [10].

It is important to note at this point a closely related theoretical result. In a scattering investigation [11] of the *strength* of the dipolar backflow pattern around a slow charged particle, the following expression for this strength (denoted here as H) was deduced:

$$H = F_s(k_{\mathrm{F}}) + \frac{4}{\pi}\sum_{\ell=0}^{\infty}(\ell+1)^2\,\sin\delta_\ell\sin\delta_{\ell+1}\sin(\delta_\ell - \delta_{\ell+1}). \tag{6}$$

This H is a multiplying factor in the distance- and velocity-dependent dipolar flow around the particle. In the perturbatively valid dielectric theory of screening the strength H is equal [11] to the embedded ionic charge due to a complete shielding in metals. The dipolar backflow represents an averaged induced current *far* from the impurity [12]. It is the far character of the backflow which makes it quite different from the wind force of equation (1). That force depends on the short-range character of the effective interaction due to an $(1 - \cos\vartheta)$ weighting of scattering to get the transport cross section. Notice that the above equations require phase shifts *solely* at the Fermi energy where the allowed excitations are.

Our goal is achieved by implementing equations (4)–(6) with scattering phase shifts based on different representations of the effective potential. In particular, the role of population of a bound state in the complete screening cloud is discussed in a comparative way. This is a key factor that influences a reliable calculation for ions migrating in an electron gas. Our nonperturbative calculation, performed within the standard Kohn–Sham procedure for screening of a proton in a paramagnetic electron gas, results in a sign-change effect for the direct charge at lower densities. The self-consistent calculation with a *prescribed* single occupancy for the bound state gives positive values for this charge in the same limit. A remarkably constant value, around unity, is established for the direct charge with a consistent calculation based on a dipolar constraint $H = Z$, using scattering states solely. In order to go beyond earlier estimations [6, 7] without a bound state, we add for comparison results for square-well models *accommodating* one bound state.

This paper is organized as follows. The different potentials used are described in section 2. The obtained results are exhibited in section 3. Finally, section 4 is devoted to a short summary. We use Hartree atomic units, $e^2 = \hbar = m_e = 1$, throughout this work.

2. Potentials

The self-consistent calculations rest on the Kohn–Sham method of density-functional theory (DFT), which reduces the complicated many-body problem of the inhomogeneous electron gas (in the presence of an embedded charge) to a single-particle problem [13]. Thus the single-particle potential energy, $v(r)$, has the following form in the present problem:

$$v(r) = -\frac{Ze^2}{r} + \int \mathrm{d}^3\mathbf{r}'\frac{\Delta n(r')}{|\mathbf{r}-\mathbf{r}'|} + \Delta v_{\mathrm{xc}}[n(r)], \tag{7}$$

in which $\Delta n(r)$ is the total-screening density. The induced exchange–correlation potential term, $\Delta v_{\mathrm{xc}}[n]$, is expressed as $\Delta v_{\mathrm{xc}}[n] = \mu_{\mathrm{xc}}(n_0 + \Delta n) - \mu_{\mathrm{xc}}(n_0)$, via an input exchange–correlation chemical potential (μ_{xc}). This form for $\Delta v_{\mathrm{xc}}[n]$ is prescribed by a physical constraint on the effective potential energy. It must vanish at infinity.

For a given density [$n_0 = 3/(4\pi r_s^3)$] of the screening environment, and depending on the magnitude of the attractive ($Z > 0$) embedded charge, the total density consists of bound and scattering eigenstates. The total density, $n(r) = n_0 + \Delta n(r)$, is constructed by summing over occupied bound and scattering states with the outgoing ($\psi_{\mathbf{k}}^+$) boundary condition

$$\psi_{\mathbf{k}}^+(\mathbf{r}) = 4\pi\sum_{\ell m} A_\ell(k)\,R_\ell(k,r)\,Y_{\ell m}(\hat{r})\,Y_{\ell m}^*(\hat{k}), \tag{8}$$

in which $R_\ell(k,r)$ are self-consistent solutions of the radial Kohn–Sham equations with $v(r)$ at $k^2/2$ scattering energy and $A_\ell(k) = i^\ell\,\mathrm{e}^{\mathrm{i}\delta_\ell(k)}$. For the sake of completeness we mention that these states have been used also in the derivation of equation (4) from (2). Here, these continuum states are

normalized on the k scale and thus the scattering (sc) part of the induced density comes, in the KS method, from an integral over the ideal Fermi–Dirac distribution function:

$$\Delta n_{\rm sc}(r) = \frac{1}{\pi^2}\sum_{\ell=0}^{\infty}(2\ell+1)\int_0^{k_{\rm F}} {\rm d}k\, k^2\left[R_\ell^2(k,r) - j_\ell^2(kr)\right]. \tag{9}$$

The total-screening condition, $4\pi\int_0^\infty {\rm d}r r^2\Delta n(r) = Z$, implies the Friedel sum rule of scattering phase shifts in one-electron mean-field treatments:

$$Z = \frac{2}{\pi}\sum_{\ell=0}^{\infty}(2\ell+1)\,\delta_\ell(k_{\rm F}) - \frac{2}{\pi}\sum_{\ell=0}^{\infty}(2\ell+1)\,\delta_\ell(0) + N_{\rm b}, \tag{10}$$

in which $N_{\rm b}$ refers to the number of occupied bound states. The rule is satisfied, of course, at numerical self-consistency of iterations. It expresses, in an independent particle picture, the fact of classical-field theory that no macroscopic electric field exist within a metal. The derivation of equation (10) for a static-impurity case rests on particle conservation for the charge, i.e. in a scattering formulation with outgoing boundary conditions the flux of a vector $J \equiv {\rm Re}[{\rm i}(\psi_{\mathbf{k}}^+)^*\nabla\psi_{\mathbf{k}}^+]$ across a closed surface is zero. This constraint eliminates [14] the next-to-leading term from the asymptotic expansion of the scattered wave and only the leading term remains, to be used in a k-averaging as in equation (10). The next-to-leading term is important in the derivation [11] of the backflow strength, as we outline below.

For ground-state calculations, on which the present work is partly based, the last two terms in equation (10) cancel each other according to Levinson's theorem. Clearly, in contrast to equations (4) and (6) where only phase shifts at $k_{\rm F}$ are needed, equation (10) contains the strong influence of the $k = 0$ limit via the last two terms. In other words, a certain charge-state-fixing (for $Z > 0$) is inherent [11] in this standard mean-field method for occupied states. Practically, at metallic densities, already the first few phase shifts provide a very accurate approximation in the case of embedded unit ($Z = \pm 1$) charges [15, 16].

It is well known that all stationary properties of metals which can be described in terms of the scattering of conduction electrons are (π) periodic functions of the phase shift, except, curiously, the Friedel sum rule. In order to remember the derivation of this sum rule we add here the *exact* derivative expression [17] via the (complex) scattering amplitude $f(k,\theta)$:

$$\frac{2\pi}{k^2}\frac{\rm d}{{\rm d}k}\left[\sum_\ell(2\ell+1)\,\delta_\ell\right] = \frac{2\pi}{k^2}\frac{\rm d}{{\rm d}k}[k\,{\rm Re}\,f(k,\theta=0)] + \frac{\rm i}{2}\int {\rm d}\Omega\left(f\frac{\partial f^*}{\partial k} - f^*\frac{\partial f}{\partial k}\right), \tag{11}$$

in which ${\rm d}\Omega = 2\pi\sin\theta\,{\rm d}\theta$ and $k\,{\rm Re}\,f(k,\theta = 0) = (\pi/2)F_s(k)$ of equation (5). In a perturbation expansion for the scattering amplitude the second term is third order in a small charge. This *order* estimation is not in contradiction with equation (6) for H in the perturbative limit. We stress at this important point that the second term in equation (6) arises from an interference ($\sim 2\,{\rm Re}\,f^* f_2$) between the first ($f$) and the next-to-leading (f_2) contribution to the outgoing wave [11]. The dipolar backflow, which rests on the particle-conservation equation [12] for the charge *and* current induced in the electron gas, depends on these details.

In a ground-state calculation for a paramagnetic host with embedded proton, a bound state appears at about $r_s \geqslant 2$, and this state is occupied by two electrons. This occupancy is prescribed [18, 19] by the analytical (smooth) behavior of the total density in the applied Hartree-like treatment. We also perform a so-called forced calculation, in which the Kohn–Sham bound orbital is occupied by one electron only. The continuum orbitals are still degenerate in spin. This is the treatment which was applied earlier [20] to the screening of a proton. We stress the point that our forced calculation, in which one has $Q = Z + 1$ for the left-hand side of equation (10) since $N_{\rm b} = 1$ in this case (if the bound state exits) by constraint, is devoted to a *demonstration* of the important role of an occupancy to our H and $Z_{\rm d}$. Another path to force a single occupancy around an embedded proton could be based on a spin-polarized hypothetical model [21]. We shall not investigate this version in the present paper since we are interested only in general statements based on forced calculations.

In order to make our comparative study more complete we use in addition a well-motivated (see below) Hulthen-type model potential [22]:

$$v(r) = -Z\frac{\Lambda}{{\rm e}^{\Lambda r} - 1}, \tag{12}$$

in which Λ is the screening parameter to be determined. We restrict ourselves to the case when $k_{\rm F} = (9\pi/4)^{1/3}/r_s$, i.e. to the paramagnetic electron gas. Using the first term for the right-hand side of equation (10) and, as a second option [23, 24], the complete equation (6) as a possible rule [11] with the $H = Z$ constraint, we determined the $\Lambda(r_s)$ parameters for both cases considering only scattering states, by using the experimental fact [25] that no muonium state is observed in μSR measurements for the Knight shift in *real* metallic targets.

The above model potential has a normalizable bound state for $\Lambda < 2Z$ and the analytical 1s-type wavefunction (a motivation to apply the Hulthen potential) is as follows:

$$\psi_0(r) = \sqrt{\frac{Z(4Z^2-\Lambda^2)}{4\pi}}\,\frac{{\rm e}^{-Zr}}{\Lambda r}\left({\rm e}^{\Lambda r/2} - {\rm e}^{-\Lambda r/2}\right). \tag{13}$$

The corresponding binding energy, i.e. the sum of the expectation values of kinetic and potential terms, is $E_0 = (1/8)(4Z^2 - \Lambda^2) - (Z/2)(2Z - \Lambda) = -(2Z - \Lambda)^2/8$ in our units. *Both* terms vanish at the critical screening, $\Lambda_{\rm cr} = 2$ for a proton. The radial density distribution, given by $4\pi r^2[\psi_0(r)]^2$, flattens with growing Λ. Surprisingly, the position of its maximum, at $r_{\rm m} = (1/\Lambda)\ln[(2Z + \Lambda)/(2Z - \Lambda)]$, shows only a very moderate increase with increasing screening. The bound state wavefunction does not delocalize appreciably until its binding energy is almost zero. It is the density reduction in $[\psi_0(r)]^2$ around a screened proton which allows, in a *real* target, an efficient electrostatic action of the surrounding lattice

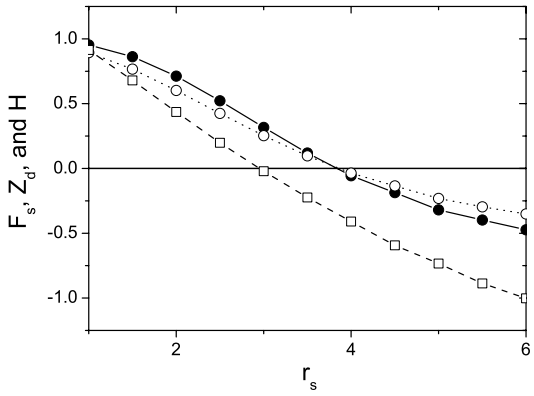

Figure 1. The F_s, H and Z_d quantities for an embedded proton, $Z = 1$, as a function of the density parameter $r_s \in [1, 6]$. The term F_s, and the complete expression, denoted by Z_d in equation (4), are presented by open circles and squares, respectively. The filled circles show the results for the strength H of the dipolar backflow given by equation (6).

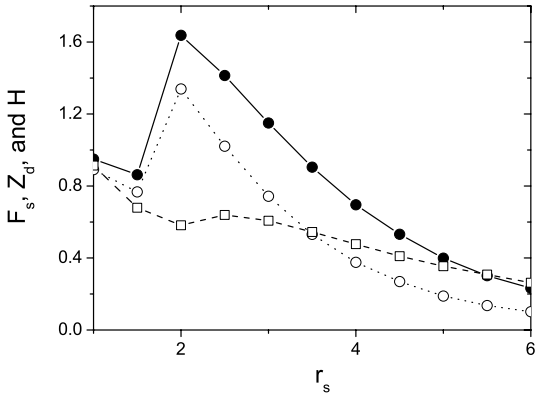

Figure 2. The F_s, H and Z_d quantities for an embedded proton, $Z = 1$, as a function of the density parameter r_s. These quantities are based on a self-consistent forced calculation. The same notations as in figure 1 are used.

ions against binding by sampling this distorted bound state. The exact form of a bound state wavefunction is crucial, for example, in the calculation of capture–loss rates for a moving proton [26] in metals, and might be useful in other transport-related problems.

Because the original expression, equation (2), for Z_d^S can be evaluated for square-well potentials only, as was shown by Sorbello, and because till now such potentials were designed without a bound state, we also calculate results for a square well with one bound state [6, 7]. The width r_0 of the square-well potential is chosen to be equal to the Thomas–Fermi screening length $1/\lambda$, where $\lambda = (4k_F/\pi)^{1/2}$. The corresponding well depth V has been determined earlier always 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. We shall use potentials with V/V_c equal to 1.3 and 1.6 in the present comparative study.

3. Results

Based on the calculated phase shifts for a paramagnetic host, figure 1 shows the F_s, the Z_d and the H quantities as a function of the density parameter r_s. As for all our results, we have a $Z = 1$ embedded charge, in order to model a proton as correctly as possible. It is seen that, in the commonly applied *ground-state* modeling, Z_d becomes negative at about $r_s \approx 3$. The calculated quantities show an 'effective-antiproton' nature. This is in harmony with the observed [16, 27] similarity of induced densities *far* from unit charges $Z = \pm 1$. We add here, for completeness, that a similar sign-change effect was found in a recent DFT calculation for the dipolar backflow strength around an embedded proton in two-dimensional paramagnetic electron gases [28]. Via the derivative (second) term for Z_d in equation (4), a weighted change in the density-of-states gives a strong effect already at a relatively high density of the host system. For a free-electron metal, say Al with $r_s \simeq 2$, the deviations from unity are notable. We attribute the somewhat surprising, negative character at lower densities of the electron gas to the fine details of the complete screening cloud.

It is well known, of course, that DFT observables are integral quantities of the Kohn–Sham wavefunctions (charge density) and eigenvalues (total energy), with the individual orbitals having little meaning [13]. Despite the virtue of the method of allowing a mathematically unambiguous definition of the bound electronic orbital, the relevance of this state to the physical excitation spectrum, at the embedding of a charge into an electron gas, is uncertain [19]. For bound orbitals, there is the problem of the self-interaction correction [29]. The proper consideration of its interplay, even only *energetically*, with the locally treated exchange–correlation is beyond the scope of the present work. The example of a *free* hydrogen atom, where the true exchange *potential* should cancel exactly the Hartree potential since an electron sees only the bare proton [30], heralds that care would be needed in a wavefunction-governed attempt.

On the other hand, a question arises regarding the direct charge. For a doubly populated bound state one expects a value of $Z_d \approx -1$, which value is taken not earlier than in the limit of a very dilute system with $r_s = 6$. This question returns even more importantly if one looks at the results obtained with a forced calculation shown in figure 2. Apparently, the effect of forcing the population is that there is no sign change. However, for $r_s \geqslant 2$ one bound electron makes the proton effectively a neutral entity and one would expect values for Z_d around zero. It seen that positive values are found for all densities. This means that one might wonder whether the formalism developed in the literature is complete for systems with a bound state. This point requires further research.

The constrained values of the screening parameter in the Hulthen model are plotted in figure 3, by open (Friedel constraint) and filled (Zwerger constraint) circles as a function of the density parameter r_s. In the former case the potential is quite rigidly localized, while in the other case it is more extended. The curve of open circles has a minimum at around $r_s = 4$ at which the above-given binding energy, E_0, would show its *deepest* (very small) value, in agreement with earlier statements [19, 31]. On the other hand, the curve of filled

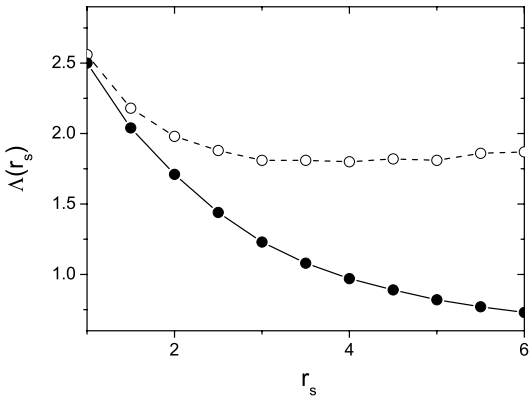

Figure 3. The screening parameters, $\Lambda(r_s)$, as a function of the density parameter r_s. Open and filled circles refer, respectively, to the Friedel and Zwerger constraints.

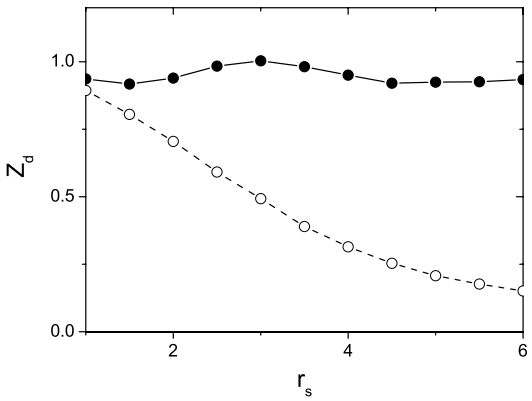

Figure 4. The direct charge, Z_d, as a function of the density parameter r_s. The results are based on phase-shift calculations with the model (Hulthen) potential to which the screening parameters are plotted in figure 3. Open and filled circles refer to the Friedel and Zwerger constraints.

circles could suggest a monotonic change in E_0 by growing r_s of the jellium system.

Based on such fixed potentials, the phase-shift-based results for the Z_d quantity are exhibited in figure 4 by two curves (open and filled circles), respectively. The direct charge remains positive in these cases, but only the backflow-based construction (see equation (6) as constraint $H = Z$) results in a surprisingly constant value (filled circles) around *unity* for the $Z = 1$ embedded charge. This is not, numerically, in disagreement with the statement [4] of Sham. He argued, using a perturbative field-theory method, that the direct force cannot be screened by the electron gas. We note at this important point that the calculation of Knight shifts for metals based on the backflow constraint ($H = Z$) to a Hulthen-type potential gave an impressive agreement with experimental data [23]. The explanation on agreement resides in the *proper* value of the enhancement factor, $E(k_F) \equiv [R_0(k_F, r = 0)]^2$. This is the key physical quantity in the μSR method, since the shift of the magnetic resonance frequency of the heavy lepton (μ^+) is proportional to $E(k_F)$.

In the model calculations of the past the formation of a bound state was avoided systematically [6, 7]. Now it becomes

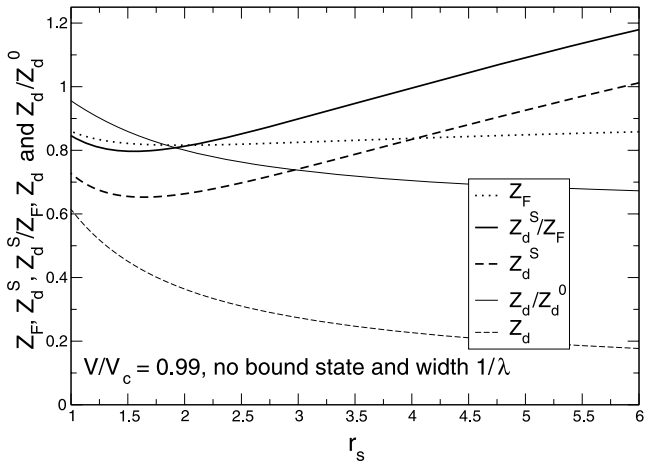

Figure 5. Results for a square well without a bound state. The Friedel sum Z_F, the Sorbello Z_d^S and the Z_d according to equation (4), which depends on the phase shifts, are plotted, including the ratios Z_d^S/Z_F and Z_d/Z_d^0.

interesting to allow for a bound state and to see what it brings about. By that also the difference between the quantities Z_d^S and Z_d of equations (2) and (4) can be seen, because both quantities can be evaluated for square-well model potentials. Further we follow Sorbello, in that he considered the ratio Z_d^S/Z_F as being a better measure for the direct charge than Z_d^S itself. The reason is that square-well potentials lead to a certain value, Z_F, for the Friedel sum which is not necessarily equal to unity. It is the merit of our self-consistent potentials that $Z_F = 1$ can be used as a constraint. It should be mentioned here that both Sorbello and one of the present authors gave values for the ratios only [6, 7]. In the same spirit we will display both Z_d and Z_d/Z_d^0, in which Z_d^0 is given by [7]

$$Z_d^0 = -4\pi\sqrt{\epsilon_F}V_{kk}. \tag{14}$$

It may be helpful to know that for a screened Coulomb potential $-Z_i e^{-\lambda r}/r$ the quantity Z_d^0 appears to be equal to the charge Z_i, which is unity for a proton.

The results for square-well potentials with the ratio V/V_c equal to 0.99, 1.3 and 1.6 are shown in figures 5–7. It is clear that the latter two potentials accommodate one bound state. The bound state energies are shown explicitly as dashed–dotted lines. The dotted lines show an increasing Friedel sum for increasing depth of the potentials. Because the solid lines are considered as the proper measure for the direct charge, the results of figure 5 confirm earlier findings, that the screening of the direct charge is relatively small, at most of the order of magnitude of 25%. Further it is seen that the Z_d curve lies clearly below the Z_d^S curve, which difference is reduced if one compares the ratios. This difference is due to the fact that equation (4) has been derived from equation (2) by using scattering states [7]. For the potentials with a bound state, figures 6 and 7, the screening does not increase much. For the $V/V_c = 1.3$ potential the relevant curves remain positive for all densities, although the Z_d/Z_d^0 curve decreases to smaller values for $r_s \to 6$. For the $V/V_c = 1.6$ potential the Z_d^S/Z_F curve still lies way above the $Z = 0$ axis, while the Z_d/Z_d^0

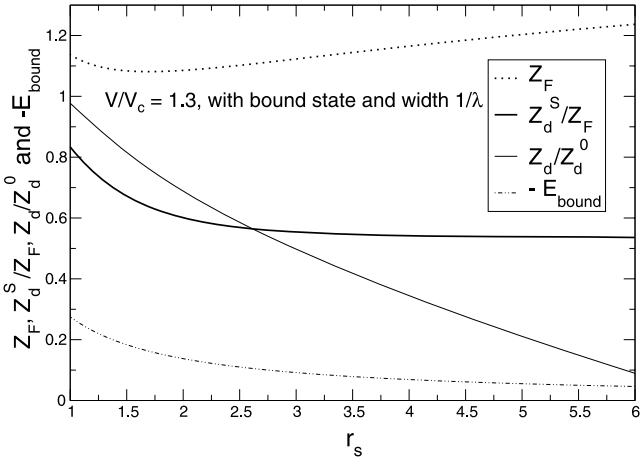

Figure 6. Results for a square well with a bound state, with $V/V_c = 1.3$. In addition to Z_F and the relevant ratios, the bound state energy is plotted.

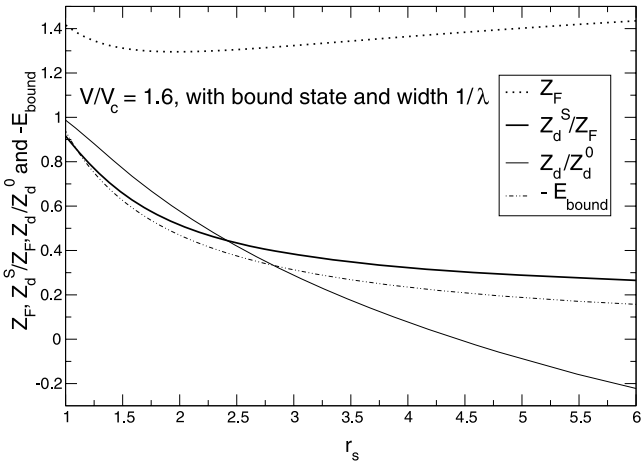

Figure 7. Results for a square well with a bound state, with $V/V_c = 1.6$; see further figure 6.

curve becomes negative at $r_s \approx 4.5$. So the question regarding the completeness of the formalism can be raised here as well.

There is a consensus between theories on electromigration that the wind force is proportional to the momentum-transfer (transport) cross section

$$\sigma_{tr}(k_F) = \frac{4\pi}{k_F^2} \sum_{l=0}^{\infty} (l+1) \sin^2[\delta_l(k_F) - \delta_{l+1}(k_F)]. \qquad (15)$$

Our final figure, figure 8, shows the important $S(k_F) \equiv [k_F^2/(4\pi)]\sigma_{tr}(k_F)$ quantity for all potentials investigated in the present comparative study. The differences are moderate, and are within the experimental ($1.5 < r_s < 3$) uncertainty, $\pm 15\%$, in stopping powers (dE/dx) at low speed (v) of penetrating protons [32]; $(dE/dx) = v(4k_F^2/3\pi)S(k_F)$. As we pointed out earlier in this paper, the above cross section depends on the $(1 - \cos\vartheta)$ weighting of the differential cross section which results in the appearance of phase-shift differences. More physically, this difference is mediated by the gradient of the potential field, and this is similar to a Coulombic one

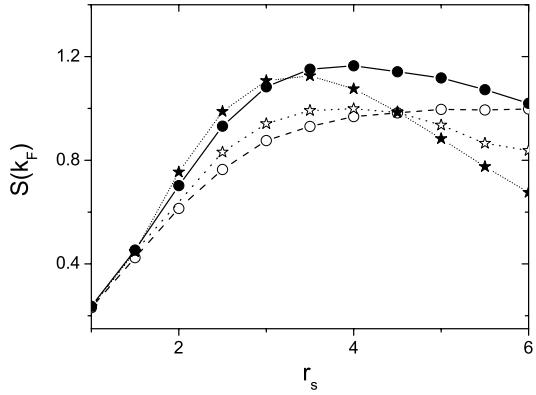

Figure 8. The reduced quantity $S(k_F) = [k_F^2/(4\pi)]\sigma_{tr}(k_F)$, as a function of the density parameter r_s. The filled and open circles refer to calculations which are based on the Hulthen potential, with the Zwerger and Friedel constraints for scattering states, respectively. Open stars are used to plot the result based on the ground-state Kohn–Sham treatment for a paramagnetic host. For the same system, filled stars denote the results of a forced calculation. See the text for further details.

at short-range. With a bare Coulomb (C) potential one has $[\delta_0^C(k_F) - \delta_1^C(k_F)] = \arctan(Z/k_F)$ for the *dominating* difference of phase shifts. This factor is behind the mentioned moderate nature of differences for $Z = 1$, despite the very different screenings at long range.

4. Summary

The magnitude of the direct charge, needed for a theoretical characterization of the driving force on an atom migrating under the influence of an applied electric field in a metal, is investigated in a comparative way. Different physically motivated representations for the effective screened potential are applied to establish a clearly understood phenomenology. It is found that the standard self-consistent procedure gives, for a paramagnetic electron gas, a sign-change effect in the direct charge. We attribute this effect to the double occupancy of the Kohn–Sham bound state which, at far distances from the impurity, results in an effectively antiproton character in density modulation.

An additional self-consistent calculation, with a forced single occupancy in the bound state, gives no sign-change effect. A consistent calculation, performed via a backflow-mediated constraint for screening and without ($H = Z$) a populated bound state, yields a value of almost unity for the direct charge of the proton over the whole *metallic* range. However, because one would expect much lower and even negative values for Z_d if the proton accommodates one or two bound electrons, the question is raised whether the formalism developed in the literature is complete. It might be that a revision is required as soon as a bound state shows up. This important question is supported by square-well model results for potentials with a bound state. This certainly will be a point of attention in further research to establish an *average* value for the direct charge which is experimentally accessible. The proper discussion of physically allowed electronic structures

of a diffusing heavy entity in electromigration would require the consideration of effects related to the local chemical environment. Notice that, although no experimental signal for muonium has been found in metals, bound states might exist. They would give rise to a certain (Korringa-type) relaxation which is not observable with muon spin resonance since the corresponding relaxation time is too long [26]. A related consideration [33] on the site preference of hydrogen in real metals suggests the screened proton, hydrogen, and spin-compensated H^- for charge states depending on the diffusion path.

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