Extending Linear Response: Inferences from Electron-Ion Structure Factors

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Linear response methods applied to electron systems often display a level of accuracy which is notable when viewed in terms of the strengths of perturbing interactions. Neglect of higher response terms is, in fact, justifiable in many cases, and it can be shown to stem from an intrinsic interference between atomic and electronic length scales. For fluid metallic systems it can be further shown that electron-ion structure (increasingly accessible experimentally) can be understood from an application of *linear response* in the electron system, combined with hard-sphere-like correlation for the ionic component. [S0031-9007(98)07697-2]

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The nearly free-electron (NFE) approximation underlies much of our understanding of the properties of condensed matter, in particular, simple metals. While *ab initio* simulation techniques have long superseded the NFE approximation in quantitative accuracy, it remains an important source of insight and of simplifying concepts to elucidate qualitative trends across different materials. It also provides guidance in situations that remain out of the reach of computational *ab initio* techniques [1]. For many years, the density $\rho^{\mathrm{ind}}(\vec{k})$ of an initially uniform electron gas induced by an embedded pseudopotential $v^{\mathrm{ps}}(\vec{k})$ has been successfully treated at linear order even though $v^{\mathrm{ps}}(\vec{k})$ is not necessarily a small perturbation. The linear approach is a key component in many applications of the NFE approximation, examples of which include pseudopotential calculations of the free energy of simple metals, their relative structural stability (and corresponding cohesive properties), and also the determination of effective ion-ion potentials [2–5]. The accuracy of the latter is a particularly striking example of the efficacy of linear response; while the energy scale of unscreened ions at typical separations is of the order of Ry, linear screening leads to ion-ion potentials fully capable of describing observed structural phase transitions and implying consequent energy scales of the order of mRy.

Here we address the evident success of the linear approximation which to date remains incompletely resolved. We show that the implied neglect of higher order response is supported by physical arguments. In particular, we explicitly demonstrate that the nonlinear terms are small for specific cases, and give arguments to suggest that this may be expected to hold more generally, the main exception being hydrogen. As an application of the underlying argument, but one with experimental consequences, we demonstrate that simple linear-response theory augmented by a hard-sphere approximation for ionic structure leads to a quantitatively accurate analytical representation of electron-ion structure factors $S_{ei}(k)$ in liquid metals, these now in principle accessible through recent advances in both neutron and x-ray scattering techniques. Another route to effective electron-ion interactions therefore opens, but here through the fluid state.

To begin, consider the response of the interacting electron gas to a single ion, where the electron-ion interaction is modeled by a *pseudopotential*, taken as a simple local one-parameter empty-core form [6]; i.e., $v^{\mathrm{ps}}(k) = -(4\pi e^2/k^2)\cos(kR_c)$, where the *atomic* core radius R_c or equivalently the zero crossing $k_0 = \pi/2R_c$ is typically fixed by an atomic property such as the ionization energy (or by a measurable crystalline metallic property such as the Fermi surface [7]). The pseudopotential leads to a local electron density inhomogeneity representable by $\rho^{\mathrm{ind}}(k)$. There are two routes to represent this induced density, the first (essentially exact) from solving the familiar self-consistent Kohn-Sham equations within the local density approximation (LDA) [8], and the second from the standard expansion of the response in powers of the perturbing (pseudo) potential, i.e.,

$$\rho^{\mathrm{ind}}(k) = \chi_1(k)v^{\mathrm{ps}}(k) + \sum_{\vec{k}_1}\sum_{\vec{k}_2}\chi_2(k,k_1,k_2) \times v^{\mathrm{ps}}(k_1)v^{\mathrm{ps}}(k_2) + \ldots . \tag{1}$$

Here the response functions $\chi_n(k_1,\ldots)$ are properties of the *homogeneous* interacting electron gas, the first being the well known linear-response function [5]. The second is given by

$$\chi_2(k_1,k_2,k_3) = [\chi_2^0(k_1,k_2,k_3) + \tfrac{1}{2}\,\mu_2(k_1,k_2,k_3)\chi_1^0(k_1) \times \chi_1^0(k_2)\chi_1^0(k_3)]/\epsilon(k_1)\epsilon(k_2)\epsilon(k_3)\,, \tag{2}$$

where $\epsilon(k)$ is the usual dielectric function: $\epsilon(k) = 1 - [4\pi e^2/k^2 + \mu_1(k)]\chi_1^0(k)$. In (2) the $\chi_n^0(k_1,\ldots)$ are the noninteracting response functions (known to second order [9]) and the $\mu_n(k_1,\ldots,k_{i+1})$ are the homogeneous limits of the nth functional derivatives of the exchange-correlation potential with respect to density. In particular, $\mu_1(k)$ is related to the spin-averaged local field correction

(LFC), $G(k) = (k^2/4\pi e^2)\mu_1(k)$. Figure 1 compares the full nonlinear LDA response and Eq. (1), taken to second order; note that Eq. (1) appears to capture most of the complete response with considerable accuracy.

Interestingly enough, the combined effects of exchange and correlation partially cancel between first and second order. In addition, the second order response contribution is of the same scale as the effect of local field corrections at first order [10]. This has important implications for the widespread application of linear response theory in the derivation of effective ion-ion potentials in (simple) metals; *the neglect of higher order response results in an overestimate of the role of exchange and correlation.* The accuracy of the second order response depicted in Fig. 1 also implies that the use of more accurate LFC's could, in some cases, lead to an improvement in accuracy over a full Kohn-Sham LDA calculation. Although much effort has gone into obtaining LFC's beyond the $(k = 0)$ LDA limit at linear order [11], the second order LFC, directly related to $\mu_2(k_1, k_2, k_3)$, to date remains unknown beyond the LDA form. However, the second order electron LFC is the direct analog of the third order direct correlation function $c^{(3)}(k_1, k_2, k_3)$ of classical liquid-state theory for which various successful approximations based on lower order correlation functions have been derived [12]. (Since the electron liquids are more weakly correlated than their classical counterparts [13], it might now be suggested that application of these classically inspired approaches to the electronic case would be useful.)

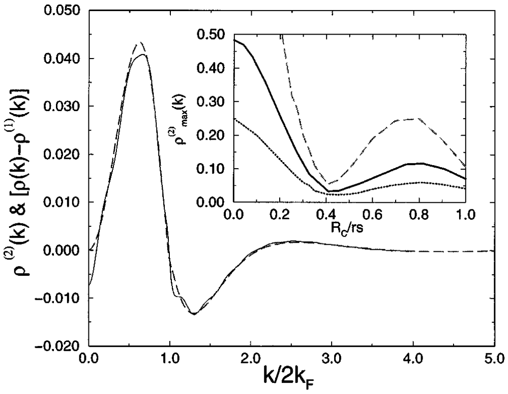

FIG. 1. A comparison of full nonlinear LDA response $[\rho(k) - \rho^{(1)}(k)]$ (solid line) to second order LDA response (dashed line) for an empty core pseudopotential with $R_c = 1.5a_0$ embedded in an electron gas with density parameter $r_s = 3a_0$. For the scale, compare this to the full response with the limit $\rho(k \to 0) = 1$. The higher order response is of the order of a few percent of the full response. In turn, the second order response captures almost all the nonlinear response. (The small difference at $k \to 0$ is a numerical artifact stemming from the use of a large but finite real-space cutoff radius in the Kohn-Sham procedure.) In the inset is plotted the maximum of the 2nd order response vs R_c/r_s for $r_s = 2a_0$ (dotted), $r_s = 3a_0$ (solid), and $r_s = 5a_0$ (dashed). Note especially the minimum at $R_c/r_s = 0.41$ which corresponds to $k_0 = 2k_F$. It is reduced by an order of magnitude from the value at $R_c = 0$ (hydrogen) and is traced to an interference between atomic and electronic length scales.

A central question now arises, one whose answer is important to the proposition we make on electron-ion structure: Why is the *nonlinear* response contribution depicted in Fig. 1 evidently so small? An immediate possibility is that higher order terms in Eq. (1) are large, but actually vary in sign and therefore mutually cancel, order by order. But another is that the higher order terms are each *individually* very small. The success at the level of second order response evidently implies that the latter is the case: *We find that the response series converges very rapidly.* This might be physically anticipated since a larger atomic parameter R_c implies a smaller perturbing potential, and the nonlinear response shows a clear decline with increasing R_c. As expected, the second order response is found to be largest for $R_c = 0$ (hydrogen), but as R_c increases from zero a noticeable secondary minimum occurs when the inverse atomic length k_0 is equal to $2k_F$. For the cases plotted in Fig. 1, the secondary minimum is reduced by an entire *order of magnitude* when compared with the value calculated for hydrogen, and is typically a factor of 3 lower than the secondary maximum at larger R_c. This minimum is attributed to the following: The second order response function, $\chi_2(k, k_1, k_2)$, itself peaks when the summed arguments in (1) are close to $2k_F$ [10]. Accordingly, if the pseudopotential zero crossing k_0 is near the response peaks at $2k_F$, a maximal cancellation or *maximal destructive interference of the atomic and electronic length scales* occurs, leading to a minimum in second order response. We may now postulate that for the simple metals a similar interference effect occurs for the higher order terms of (1).

Typically the value of $k_0/2k_F$ lies between 0.75 and 1, and is therefore very close to the secondary minimum in the nonlinear response. Note that the ratio of the atomic and electronic length scales is set primarily by the volume energy terms in the total ground state energy, and is almost independent of structure [5]. This clarifies in large part why the ubiquitous linear-response approximation performs so remarkably well for many materials and why the higher order terms are indeed small. The NFE approximation has often been justified in a context far wider than linear response alone by appeal to the fact that for a crystalline solid, the structure dependent reciprocal lattice vectors are typically near the pseudopotential zero crossing k_0 with the inference that the net scattering is small [1]. This important effect stems from the confluence of an *atomic* and a *structural* length scale; the interference effect we discuss is complementary, but has a different physical origin, namely, an interference between intrinsic atomic and electronic length scales. Once again, the clear exception is the singular case of a point-charge $[v^{\mathrm{ps}}(k) \sim 4\pi e^2/k^2]$, i.e., the case of hydrogen, which has no well-defined core-length scale k_0, no oscillations in the potential, and thus no interference effect in the higher order terms. In sharp contrast to other systems, nonlinear response terms are large term by term. In fact, the response series may not even formally converge, and great care must be taken when applying concepts derived from linear-response theory to hydrogen (it is not a simple material).

As noted, the continued accuracy of linear response is important to an interpretation now proposed for electron-ion structure factors $S_{ei}(k)$ in metallic fluids, these being defined as k-space density-density correlation functions [3]. Invoking the adiabatic approximation they can always be rewritten in terms of the ion-ion structure factors as follows:

$$S_{ei}(k) = \frac{n(k)}{\sqrt{Z}} S_{ii}(k), \tag{3}$$

which defines a new dimensionless object $n(k)$. Electron-ion correlations can therefore be described by convolving the pseudoelectron density (or pseudoatom) $n(k)$ with the ionic correlations. The accuracy of linear response for the pseudopotential in an electron gas implies that it should now also be an excellent approximation for a determination of the pseudoatom density. For simple liquid metals $S_{ii}(k)$ is very well approximated by the Percus-Yevick analytic form for hard spheres by specifying a single parameter, the packing fraction η, which is close to $\eta \sim 0.46$ for most simple metals near melting [14]. Using this in (3), we compare our approach in Fig. 2 to the *full ab initio* Car-Parrinello [15] calculations of de Wijs *et al.* [16]. The correspondence is striking, especially when we note that the parameters η and R_c are *a priori* set by other physical properties (no fitting is necessary).

Besides a semiquantitative description of electron-ion structure factors, this linear response theory now provides an important qualitative insight into the form of the electron-ion structure factors [17]. The pseudoatom density $n(k)$ is typically largest for small k and rapidly declines for larger k, while the near classical ion-ion structure factor $S_{ii}(k)$ follows an inverse behavior; it is small for small k. Together with the product form (3) this implies that the shape of the electron-ion structure factor $S_{ei}(k)$ is determined primarily by the position of the *zero crossing* $\bar{k}_0$ of $n(k)$ with respect to the *first maximum* k_p of $S_{ii}(k)$. If $\bar{k}_0 < k_p$, then $S_{ii}(k)$ selects (or filters) the negative part of $n(k)$ and $S_{ei}(k)$ takes a form similar to that of Mg [Fig. 2(a)]. Conversely, if $\bar{k}_0 > k_p$, then the ion-ion structure factor selects (or filters) the positive part of $n(k)$, and again, $S_{ei}(k)$ takes a form similar to that of Bi [Fig. 2(c)]. Since $\chi_1(k)$ is positive definite, the zero crossing in linear response occurs at k_0. The large slope of $n(k)$ near the zero crossing then implies that nonlinear corrections must have a small effect on the location of the zero crossing, and together with the expected accuracy of linear response this implies that $\bar{k}_0 \sim k_0$. As mentioned earlier, for most metals, k_0 is just a little less than $2k_F$, and the latter's ratio to k_p is well known: for small valence ($Z \leq 2$), $2k_F < k_p$; for large valence ($Z \geq 3$), $2k_F > k_p$ [18]. This accounts in a straightforward way for the two separate forms found by de Wijs *et al.* [16]: For Mg, $\bar{k}_0 < k_p$ ($Z = 2$), which belongs to the *low-valence class* of electron-ion structure factors. For Bi, $\bar{k}_0 > k_p$ ($Z = 5$), and we may refer to this as the *high-valence class* of electron-ion structure factors [19]. Generally ions of valence $Z \leq 2$ belong to the low-valence class, while ions with valence $Z > 3$ belong to the high-valence class. Ions with valence $Z = 3$ typically belong to the high-valence class also, although they may be characterized by a crossover form [10]. The analytical approach above can easily be extended by using the modern theory of liquids to obtain improved ion-ion structure factors [20], but to include second order contributions to the pseudoatom $n(k)$ necessitates not only second order electron response, but also contributions from ion-ion triplet structure. This can also be carried out with concepts from the theory of classical liquids [10].

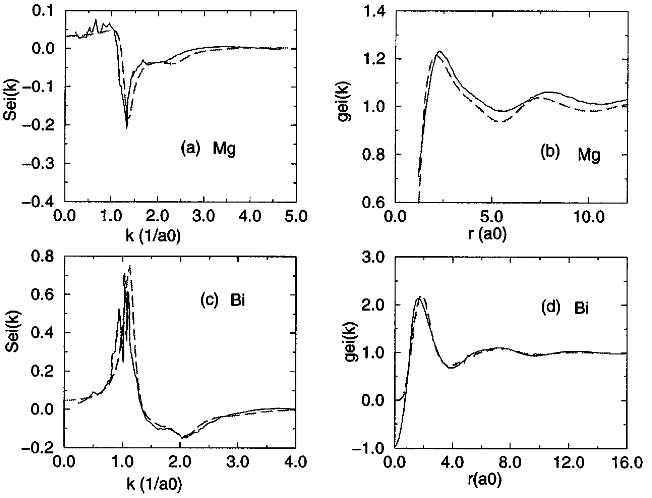

FIG. 2. The electron-ion structure factor $S_{ei}(k)$ and related electron-ion correlation function $g_{ei}(r)$ for Mg and Bi: Car-Parrinello results of de Wijs *et al.* [16] (solid line) vs the simple linear-response approach augmented by a hard-sphere approximation (dashed line). Panel (a) shows $S_{ei}(k)$ and panel (b) shows $g_{ei}(r)$ for liquid Mg. Panel (c) shows $S_{ei}(k)$ and panel (d) shows $g_{ei}(r)$ for liquid Bi. For Mg the parameters (taken from the literature) are $r_s = 2.66a_0$ and $R_c = 1.31a_0$, and for Bi the parameters (taken from the literature) are $r_s = 2.25a_0$ and $R_c = 1.15a_0$. Both have a packing fraction $\eta = 0.46$ [note that for the $g_{ei}(r)$ the region inside the core radius is not physically significant].

These observations have a potentially useful experimental consequence: The principal features of electron-ion structure factors can be measured by exploiting the differences between x-ray scattering, which probes the density fluctuations of *all* electrons, and neutron scattering which generally probes fluctuations of the nuclei [21]. X-ray measurements are usually interpreted using a free atom form factor, while our analysis suggests that for liquid metals, they should be interpreted with the pseudoatom as a form factor. When this is taken into account, a small difference between x-ray and neutron scattering determinations of the ion-ion structure factor should emerge. This difference is largest for metals with a high ratio of valence to core electrons. For Li (1:2) or Al (3:10), we predict a 2% difference at the first peak of the structure factor [22], but the largest effects are expected for Be which has the highest ratio of valence to core electrons (1:1) and for which the difference could be as much as 7%, well within experimental range. In addition, Be may straddle the two classes (k_0 is near k_p), which means that small differences in $\bar{k}_0$ with respect to k_0 may lead to significant, qualitative differences in $S_{ei}(k)$, making it a particularly interesting candidate for illuminating nonlinear effects. In a similar way we now anticipate that higher order effects can be revealed in partially covalent liquid metals, silicon and gallium being examples. The arguments presented suggest that these should become relatively less important upon an increase in density (via pressure).

The arguments and associated analysis above therefore provide a physical basis for understanding why linear-response theories in dense electron systems generally perform so well. The accuracy of linear response is demonstrated for fluid metals by a simple analytical linear-response theory augmented by a hard-sphere approach to classical electron-ion structure factors, which already gives semiquantitative accuracy. It suggests that there are two main classes of electron-ion correlation functions, one for high- and one for low-valence metals. Finally, it is suggested that experimental advances in x-ray and neutron scattering may be poised to provide measurements of these electron-ion correlation functions, and hence on a systematic exploration of the interactions themselves.

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