Extending Linear Response: Inferences from Electron-Ion Structure Factors

A.A. Louis and N.W. Ashcroft
Cornell Center for Materials Research, and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853-2501

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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 \textit{linear response} in the electron system, combined with hard-sphere like correlation for the ionic component.

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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 While ab-initio simulation techniques have long superseded the NFE approximation in quantitative accuracy, it remains an important source of insight and of simplifying concepts to elucidate qualitative trends across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. For many years, the density $\rho_{\text{ind}}(k)$ of an initially uniform electron gas induced by an embedded pseudo-potential $v_{\text{ps}}(\mathbf{k})$ has been successfully treated at linear order even though $v_{\text{ps}}(\mathbf{k})$ is not necessarily a small perturbation. The linear approach is a key component in many applications of the NFE approximation, examples of which include pseudo-potential 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. 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 $S_n(k)$ 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 \textit{pseudo-potential}, taken as a simple local one-parameter empty-core form \cite{Louis0} i.e.: $v_{\text{ps}}(k) = -(4\pi\varepsilon^2/k^2)\cos(kR_e)$, where the \textit{atomic} core-radius $R_e$ or equivalently the zero-crossing $k_0 = \pi/2R_e$ is typically fixed by an atomic property such as the ionization energy (or by a measurable crystalline metallic property such as the Fermi surface \cite{Ashcroft}). The pseudo-potential leads to a local electron density inhomogeneity representable by $\rho_{\text{ind}}(k)$. 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) \cite{Vanderbilt}, and the second from the standard expansion of the response in powers of the perturbing (pseudo)potential, i.e.:

$$\rho_{\text{ind}}(k) = \chi_1(k)v_{\text{ps}}(k) + \sum_{k_1} \chi_2(k,k_1,k_2)v_{\text{ps}}(k_1)v_{\text{ps}}(k_2) + ...$$

(1)

Here the response functions $\chi_n(k_1...)$ are properties of the \textit{homogeneous} interacting electron gas, the first being the well known linear response function \cite{Ashcroft}. The second is given by:

$$\chi_2(k_1,k_2,k_3) = \left(\frac{\chi_2^0(k_1,k_2,k_3)}{\chi_2^0(k_1,k_2,k_3) + \frac{1}{2} \mu_2(k_1,k_2,k_3)\chi_2^0(k_1)\chi_2^0(k_2)\chi_2^0(k_3)}\right) \langle \epsilon(k_1)\epsilon(k_2)\epsilon(k_3) \rangle,$$

(2)

where $\epsilon(k)$ is the usual dielectric function: $\epsilon(k) = 1 - \left(4\pi\varepsilon^2/k^2 + \mu_1(k)\right)\chi_2^0(k)$. In (2) the $\chi_n^0(k_1...)$ are the non-interacting response functions (known to second order \cite{Ashcroft}) and the $\mu_n(k_1...k_{n+1})$ are the homogeneous limits of the...
n-th 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), $G(k) = (k^2/4\pi e^2)\mu_1(k)$. Fig. 1 compares the full LDA response, and equation (1), taken to second order; note that it appears to capture most of the complete response with considerable accuracy.

FIG. 1. A comparison of full non-linear LDA response $[\rho(k) - \rho^{(1)}(k)]$ (solid line) to second order LDA response (dashed line) for an empty core pseudo-potential 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 $\rho(k=0)=1$. The higher order response is of the order of a few % of the full response and in turn, the second order response captures almost all the non-linear response. (The small difference at $k \to 0$ is a numerical artifact stemming from the use of a large but finite real-space cut-off radius utilized in the Kohn-Sham procedure.) In the insert 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.

Interestingly enough, the combined effects of exchange and correlation partially cancel between first and second order, and this implies that the neglect of the $\mu_n(k_{1,i+1})$ at both orders (the RPA) is found to be more accurate than the result obtained by merely including them at a single order only [1]. 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 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 correlations 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.)

A central question now arises (whose answer is important to the proposition we make on electron-ion structure): Why is the non-linear response contribution depicted in Fig. 1 evidently so small? An immediate possibility is that higher order terms in equation (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 2nd 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 non-linear response shows a clear decline with increasing $R_c$. As anticipated the second order response is found to be largest for $R_c=0$ (hydrogen), but as $R_c$ increases from zero a noticable 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 factor of three 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 $2k_F$. Accordingly, if the pseudo-potential zero-crossing $k_0$ is near the response peaks at $2k_F$, a maximal cancellation or maximal destructive interference of the atomic and electronic lengthscales 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 (4).

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 non-linear 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 pseudo-potential zero-crossing $k_0$ with the inference that the net scattering is small [1]. This important effect stems from the confluence 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 lengthscales. Once again, the clear exception is the singular case of a point-charge ($\nu_{ps}(k) \sim 4\pi e^2/k^2$), 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, non-linear 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:

$$S_{eI}(k) = \frac{n(k)}{\sqrt{Z}} S_{II}(k),$$

which defines a new dimensionless object $n(k)$. Electron-ion correlations can therefore be described by convolving the pseudo-electron density (or pseudo-atom) $n(k)$ with the ionic correlations. The accuracy of linear response for the pseudo-potential in an electron-gas implies that it should now also be an excellent approximation for a determination of the pseudo-atom 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 $\eta$, 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 $\eta$ and $R_c$ are a priori set by other physical properties (no fitting is necessary).
the zero-crossing then implies that non-linear corrections and together with the expected accuracy of linear response this implies that \( \bar{n} \) factor selects (or filters) the positive part of \( c \)). Since \( k \) factors. For \( B_i \), \( \bar{n} \) and \( \bar{p} \) for large valence (\cite{16}). 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 characterized by a crossover form \( \chi_1(k) \) 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 non-linear 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 \( k_0 \sim k_0 \). As mentioned earlier, for most metals, \( k_0 \) is just a little less than \( 2k_F \), and the latter’s ratio to \( k_F \) is well known: for small valence (\( Z \leq 2 \)), \( 2k_F < k_F \); for large valence (\( Z \geq 3 \)): \( 2k_F > k_F \) \cite{16}. This accounts in a straightforward way for the two separate forms found by deWijs \textit{et al} \cite{16}: For Mg, \( k_0 < k_F \) (\( Z = 2 \)), which belongs to the low valence class of electron-ion structure factors. For Bi, \( k_0 > k_p \) (\( Z = 5 \)) and we may refer to this as the high valence class of electron-ion structure factors \cite{16}. 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 characterized by a crossover form \cite{16}. The analytical approach above can easily be extended by using the modern theory of liquids to obtain improved ion-ion structure factors \cite{20}, but to include second order contributions to the pseudo-atom \( n(k) \) 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. \cite{14}

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. \cite{23}. 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 pseudatom 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 \cite{22}, but the largest effects are expected for Be which has the highest ratio

\[ S_{\alpha\beta}(k) = \frac{1}{(2\pi)^2} \int d^2 r \langle \psi_\alpha(\mathbf{r}) \psi_\beta(-\mathbf{r}) \rangle e^{i \mathbf{k} \cdot \mathbf{r}} \]

\[ R_k = \frac{1}{(2\pi)^2} \int d^2 r \langle \psi_\alpha(\mathbf{r}) \psi_\beta(-\mathbf{r}) \rangle e^{i \mathbf{k} \cdot \mathbf{r}} \]

\[ g_{\alpha\beta}(r) = \frac{1}{(2\pi)^2} \int \frac{dk}{k \sin \theta} S_{\alpha\beta}(k) e^{-ik \cdot r} \]

\[ e_i(\mathbf{r}) = \sum_{\alpha} \int d^2 r \langle \psi_\alpha(\mathbf{r}) \psi_\alpha(\mathbf{r} + \mathbf{a}) \rangle e^{i \mathbf{k} \cdot \mathbf{r}} \]

\[ m_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \int \frac{dk}{k} e^{i \mathbf{k} \cdot \mathbf{r}'} \left( \frac{1}{(2\pi)^2} \int d^2 r \langle \psi_\alpha(\mathbf{r}) \psi_\beta(\mathbf{r} + \mathbf{r}') \rangle \right) \]

\[ e_i(\mathbf{r}) = \sum_{\alpha} \int d^2 r \langle \psi_\alpha(\mathbf{r}) \psi_\alpha(\mathbf{r} + \mathbf{a}) \rangle e^{i \mathbf{k} \cdot \mathbf{r}} \]

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\[ e_i(\mathbf{r}) = \sum_{\alpha} \int d^2 r \langle \psi_\alpha(\mathbf{r}) \psi_\alpha(\mathbf{r} + \mathbf{a}) \rangle e^{i \mathbf{k} \cdot \mathbf{r}} \]
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 \( (k_0 \text{ is near } k_p) \), which means that small differences in \( k_0 \) 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 semi-quantitative accuracy. It suggests that there are two main classes of electron-ion correlation functions, one for high and one for low valence metals. Finally is it suggested that experimental ion structure factors, which already gives semi-quantitative accuracy. It suggests that there are two main classes of metals by a simple analytical linear-response theory augmented by a hard-sphere approach to classical electron-

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