Chapter 4

A Single Atom in an Electron Gas

4.1 Introduction to the Problem: Reducing the Atom to a Pseudo-Potential in Jellium

Immerse a single point charge Q into an electron gas[1]. The first Z_A electrons will get sucked into bound states[2], localized near the center of charge Q , practically oblivious to the electron gas from which they originated. Following standard usage, we shall call this new object, the potential plus Z_A bound electrons, an *ion* of valence $Z = (Q - Z_A)$. At a one-electron level, the exclusion principle requires the wave-functions of the remaining scattering state electrons to be orthogonal to the Z_A bound states, a constraint that can only be satisfied by introducing multiple nodes in the scattering state wave-functions near the ion center, implying a higher kinetic energy. Thus the scattering state electrons are effectively repelled by the

[1] With a suitable rigid charged background to insure electro-neutrality of the entire electron gas plus charge Q system

[2] This depends on the density, for high enough electron density there will be no bound states.

bound core region and the overall effect of the attractive potential is weakened. We model this by a much weaker *pseudo-potential*, that is, an electron-ion potential with ideally the same scattering properties as the full ion, but with the bound core electrons now safely tucked away into its definition and subsequently ignored[1]. In this chapter we use a simple local form which doesn't have the exact scattering properties as the full ion plus core electrons, but has only one parameter which greatly facilitates our investigations. Since where we are mainly interested in the response of an electron-gas to an atom and not details of the atoms themselves this slight loss of accuracy is not important. The most popular of these local pseudo-potentials is the the Ashcroft or empty-core pseudo-potential (APP)[3]:

$$v^{ps}(r) = \begin{cases} 0 & r < R_c \\ -2Z/r & r \geq R_c, \end{cases} \tag{4.1}$$

which in Fourier space is given by:

$$v^{ps}(k) = \int d\vec{r} v^{ps}(r) e^{i\vec{k}\cdot\vec{r}} = -\frac{8\pi}{q^2} cos(kR_c). \tag{4.2}$$

(We use atomic units throughout). The repulsive effect of the core electrons is modeled simply by setting the inner part of the Coulomb potential to zero and the single parameter, R_c, is typically fixed either by an atomic property such as the ionization energy or else by some measurable material property of the crystalline state such as the Fermi-surface if the system is metallic. It is an average representation of an ionic dimension. An important parameter related to R_c is q_0, the first k-space zero of the pseudo-potential:

$$q_0 = \frac{\pi}{2R_c}. \tag{4.3}$$

In spite of its simplicity, the APP works remarkably well, especially for simple metals, and has been the well tested work-horse of many analytical and semi-analytical theories. Other local and non-local pseudo-potentials have also been widely used, but we chose the APP primarily because of its simplicity.

Having suitably reduced the atom in an electron gas problem to an ion of valence Z, now represented by a pseudo-potential $v^{ps}(r)$, we turn to the question: "What is the total response of an electron gas to such a pseudo-potential perturbation?". Even though the bound core-states are accounted for, the pseudo-potential still attracts the scattering state electrons, resulting in a local inhomogeneity surrounding the potential an induced density $\rho(r)$ with the property:

$$\int_V \rho(r) d\vec{r} = Z, \tag{4.4}$$

i.e. the induced density has a charge equal to the ionic valence; the ion is "perfectly screened" at long range (note that the total electron density is $\rho_0 + \rho(r)$). The rest of this chapter will concern itself with ways of calculating this induced density $\rho(r)$.

4.2 Infinite Order Response within the Local Density Approximation (LDA)

The advent of the Hohenberg-Kohn theorem[5] and the associated Kohn-Sham equations[6, 7] (see also appendix C) introduced many new simplifying concepts to electronic structure theory. In particular the Kohn-Sham equations, which follow from an energy minimization principle[7], reduce the many-body interacting electron-gas problem to a one-body Schroedinger equation moving in a (self-consistent) external potential of the form:

$$v_{eff}(\vec{r}) = v^{ext}(\vec{r}) + \int \frac{2\rho(r')}{|\vec{r}-\vec{r'}|} d\vec{r'} + \mu_{xc}(\vec{r};[\rho]). \tag{4.5}$$

The first term is the external potential $v^{ext}(\vec{r})$, the second is the screened (Hartree) term due to the induced charge $\rho(r)$, and the last term is the so-called exchange correlation potential $\mu_{xc}(\vec{r};[\rho])$, which contains all the effects of correlation and exchange and into which are lumped all the complexities of the full interacting many-body problem. However, for the ground state, the Hohenberg-Kohn theorem[5] states that the exchange-correlation potential is a unique albeit unknown *functional* of the one-body density $\rho(r)$ and in fact several approximations based on this idea exist, the best known of which is the so-called local density approximation (LDA)[6, 7] which we adopt for this chapter. For a single atom modeled by a spherically symmetric pseudo-potential, the Kohn-Sham Schroedinger equation reduces to a single differential equation in the variable r, which can then be solved numerically[3], provided special care is taken to enforce the perfect-screening sum-

[3] For the case of two hydrogen atoms in an electron gas, this problem becomes considerably more complex, and various approximations must be invoked to extract a problem numerically tractable in real space; k-space methods must be used instead[11].

rule of equation (4.4). Many groups have already acquired considerable expertise in this problem[13], which forms an important input for effective medium theories of metallic bonding[12]. We adapted one version of this code by G. Eliasson and K. Jacobsen to calculate the total LDA response of an electron gas to a pseudopotential of the form given by equation 4.1. Its output is the "exact" or infinite order response.

4.3 Linear and Non-linear Response Theory

4.3.1 The general formulation of response theory

The output of the self-consistent Kohn-Sham formalism can formally be expanded in powers of the perturbing (pseudo)potential:

$$\rho(k) = \chi_1(k) v^{ps}(k) + \sum_{\vec{k}_1} \sum_{\vec{k}_2} \chi_2(k, k_1, k_2) v^{ps}(k_1) v^{ps}(k_2) + ..., \tag{4.6}$$

where the interacting response functions $\chi_n(k_1...)$ are properties of the *homogeneous* electron gas. The first two are given by:

$$\chi_1(k) = \frac{\chi_1^0(k)}{\epsilon(k)} \tag{4.7}$$

and

$$\chi_2(k1, k2, k3) = \frac{\chi_2^0(k1, k2, k3) + \frac{1}{2}\mu_2(k1, k2, k3)\chi_1^0(k1)\chi_1^0(k2)\chi_1^0(k3)}{\epsilon(k1)\epsilon(k2)\epsilon(k3)}, \tag{4.8}$$

where the $\chi_n^0(k_1..)$ are the response functions for the non-interacting case, the $\mu_n(k_1...)$ are the homogeneous limit of functional derivatives of the exchange correlation potential w.r.t. the density, and $\epsilon(k)$ is the dielectric function given by:

$$\epsilon(k) = 1 - \left(\frac{8\pi}{k^2} + \mu_1(k)\right) \chi_0^1(k). \tag{4.9}$$

More details on these response functions and their definitions can be found in Appendix D. The induced density of equation 4.6 can also be written, order by order as:

$$\rho(k) = \rho_1(k) + \rho_2(k) + \rho_3(k) + ..., \tag{4.10}$$

where each ρ_n is identified with the contributions stemming from nth order of response and obeys the perfect screening sum-rule:

$$\int \rho_n(r) d\vec{r} = \begin{cases} Z, & n = 1, \\ 0, & n > 1. \end{cases} \tag{4.11}$$

This is most easily proven in k-space. At first order, for small q, the potential scales as $\sim Z/q^2$, while the response function $\chi^1(q)$scales as $\sim q^2$. Thus the sum-rule is completely saturated at linear order in the response series. The question naturally arises: do the higher order terms *collectively* sum to zero for small q, or do they do so *individually*? If the potential is multiplied by an arbitrary factor λ, the nth term in the series (4.6) scales as λ^n. Since the sum of higher order terms must equal zero for arbitrary λ each term must *individually* be zero for $q \to 0$.

4.3.2 Linear response theory

The first term in the expansion (4.6) is the familiar linear response term:

$$\rho_1(k) = \chi_1(k) v^{ps}(k) \tag{4.12}$$

which already saturates the perfect screening sum-rule of equation 4.11 :

$$\rho_1(k = 0) = Z. \tag{4.13}$$

Note that given a choice for Z, this sum-rule sets the overall scale of linear response for all rs and R_c. In general linear response is expected to work better for small rs (high density) and large R_c (small perturbations). For large enough rs bound states set in and linear response theory breaks down [more on this later]. As demonstrated in figure 4.1 linear response works remarkably well and captures the dominant response of the electron gas, something which is not at all a-priori obvious since an atom is not generally considered a weak perturbation. It needs to be understood.

4.3.3 2nd order and full non-linear induced density

The full second order response function $\chi_2^0(q1, q2, q3)$ for non-interacting electrons was first calculated by Lloyd and Sholl[8]; their forms are used in what follows. Later

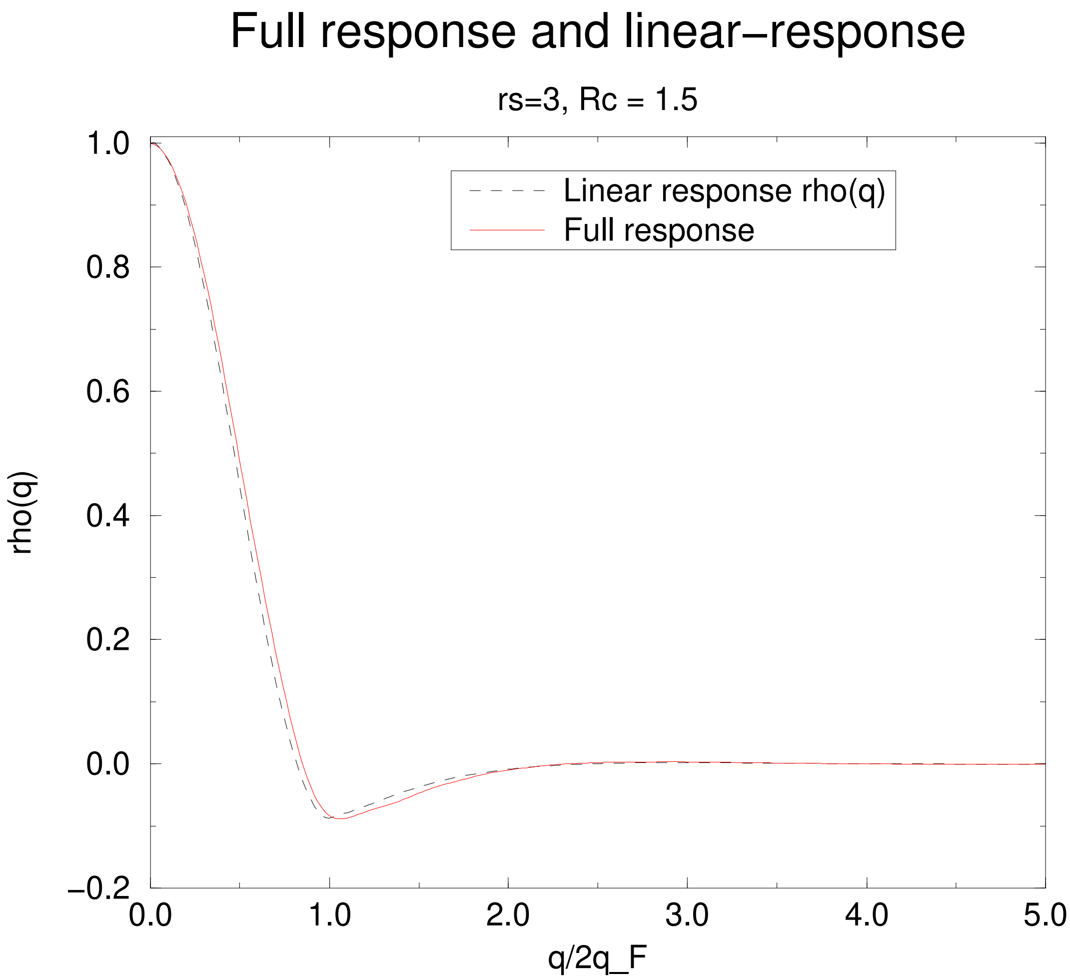

Figure 4.1: **density in k-space for an LDA embedded APP and a linear response APP**
For the density parameter $rs = 3$ and atomic APP parameter $R_c = 1.5$ are plotted the full LDA embedded APP response and the linear response. Note how well the linear response captures the full response already.

approximate forms for the 3rd and 4th order expressions were given by Hammerberg and Ashcroft[9], and also by Kagan *et. al*[10]. From equation 4.6, the second order induced density is given by:

$$\rho_2(k) = \sum_{\vec{k}_1}\sum_{\vec{k}_2} \chi_2(k, k_1, k_2) v^{ps}(k_1) v^{ps}(k_2) \tag{4.14}$$

Where $\chi_2(k, k_1, k_2)$ is the full interacting response function defined in Appendix D. Translational invariance of the unperturbed electron gas imposes on the sum a delta-function constraint of the form:

$$\vec{k} + \vec{k}_1 + \vec{k}_2 = 0, \tag{4.15}$$

so that the double sum (4.14) reduces to an integral of the form:

$$\begin{aligned}\rho_2(k) \quad = \quad & \frac{1}{(2\pi)^2}\frac{1}{k\epsilon(k)}\int_0^\infty dk_1 k_1 \frac{v^{ps}(k_1)}{\epsilon(k_1)}\int_{|k1-k|}^{|k1+k|} dk_2 k_2 \frac{v^{ps}(k_2)}{\epsilon(k_2)} \cdot \\ & \left[\chi_2^0(k_1, k_2, k_3) + \frac{1}{2}\mu_2(k1, k2, k3)\chi_1^0(k1)\chi_1^0(k2)\chi_1^0(k3)\right] \end{aligned} \tag{4.16}$$

The integrand is a product of the 2nd order density response function defined in Appendix D, and the oscillatory potential defined in equation 4.2; it is depicted in figure 4.2.

The question naturally arises: How accurate is this 2nd order response theory? Does it actually capture the most of the higher order response?

In fact, as shown in figure 4.3 and figure 4.4, the second order response result performs remarkably well, far beyond our initial expectations. When compared to the full response the maximum error is on the order of 0.5% for these conditions[4]. This calls for a more thorough exploration within the space of the atomic variable q_0 (related to R_c through equation 4.3) and the electron-gas variable $2k_F$ (twice the Fermi-wave vector k_F, related to the density parameter rs by: $k_F = 1.919/rs$).

[4] And that error may very well be due to numerical errors in truncating the Friedel oscillations

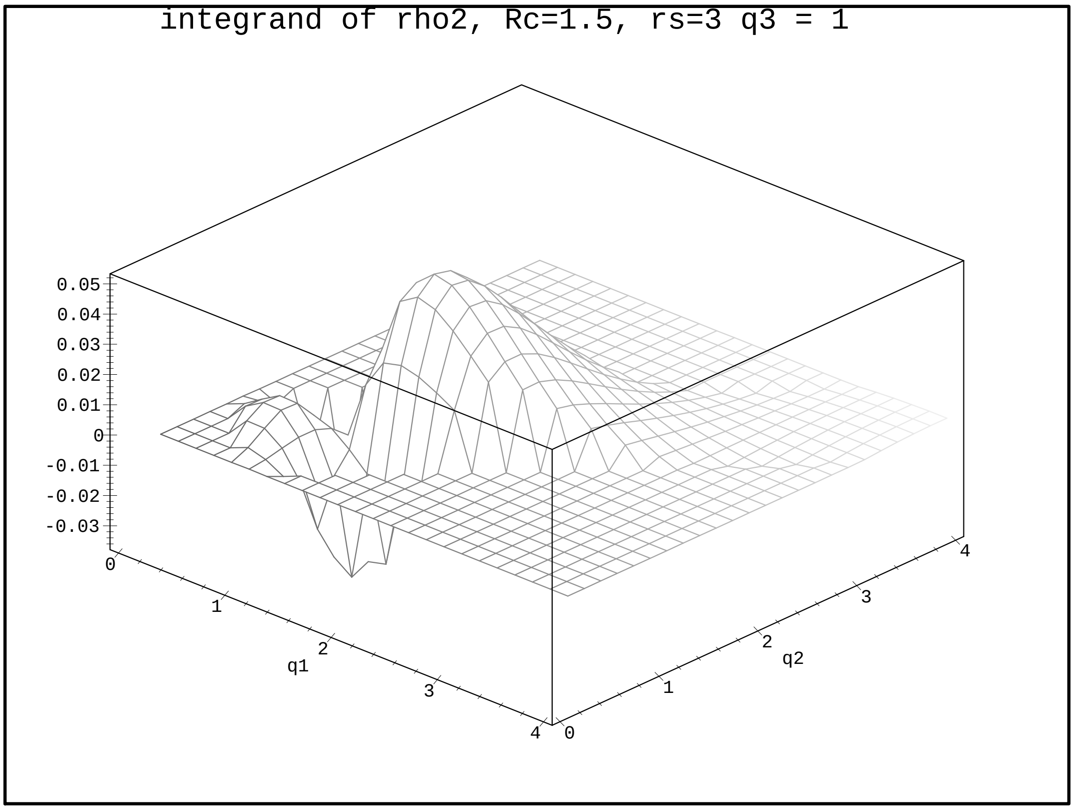

Figure 4.2: **Integrand of equation 4.16 for $k = 1, rs = 3, R_c = 1.5$.**
Note that the dominant contribution comes from wave-vector moduli near $2k_F$ and that the integration volume is restricted by the limits $(k < k_1 + k_2)$ $(k_1 < k + k_2)$ and $(k_2 < k + k_1)$ which stem from the delta-function constraint 4.15 and must be simultaneously satisfied. $2k_f = 1.28$ a.u. and $q_0 = 1.05$, and both lengthscales are visible in the integrand. Note that there is some cancellation due to the oscillation of the pseudo-potentials.

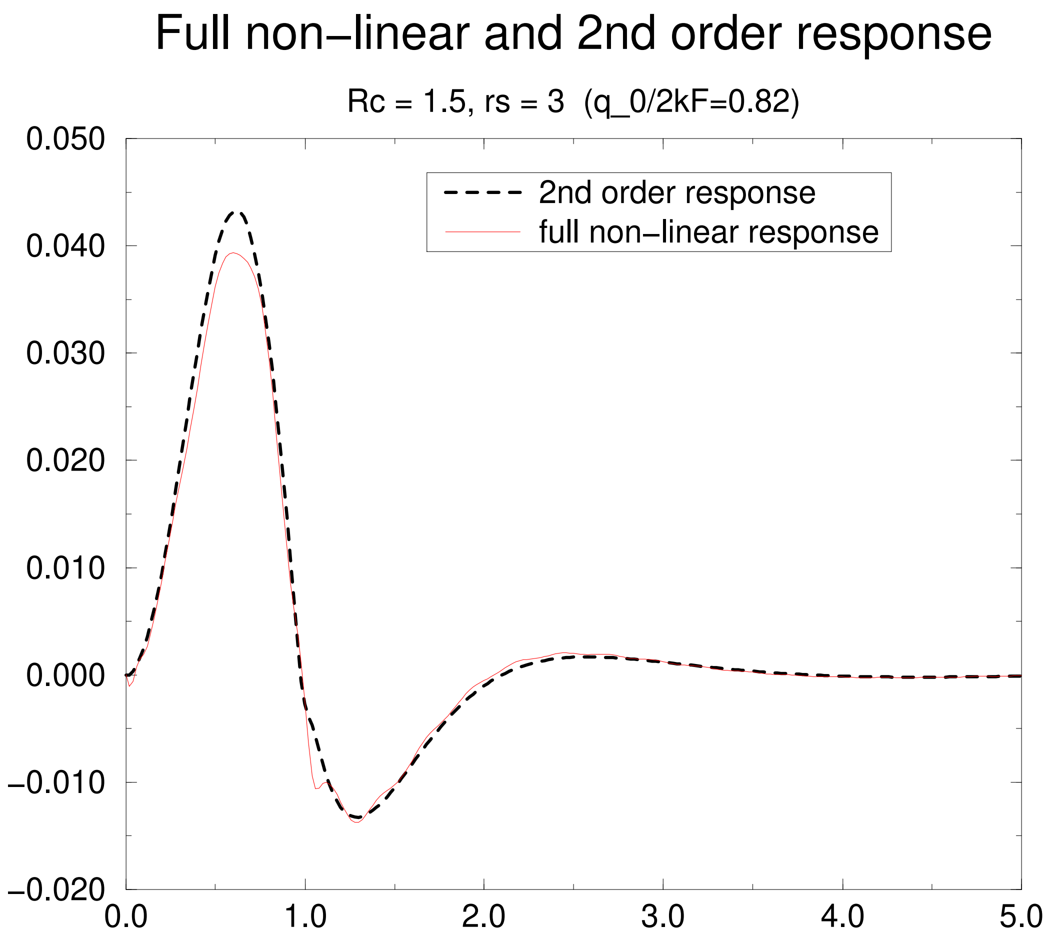

Figure 4.3: **Full non-linear LDA response :**$\rho(k) - \rho_1(k)$ **compared to the second order response** $\rho_2(k)$ **for** $rs = 3$ $R_c = 1.5$**,** $Z = 1$**.**
Compared in the figure above are the full non-linear LDA response (i.e. the infinite order summation of equation 4.6, and also the 2nd order response of equation 4.16. For the scale, compare this to the full response, which goes to $rho(q = 0) = Z$, or to the linear response depicted in figure 4.4. The LDA result has some slight numerical errors because the real-space calculations are cut-off for a certain radius and Friedel oscillations are then ignored.

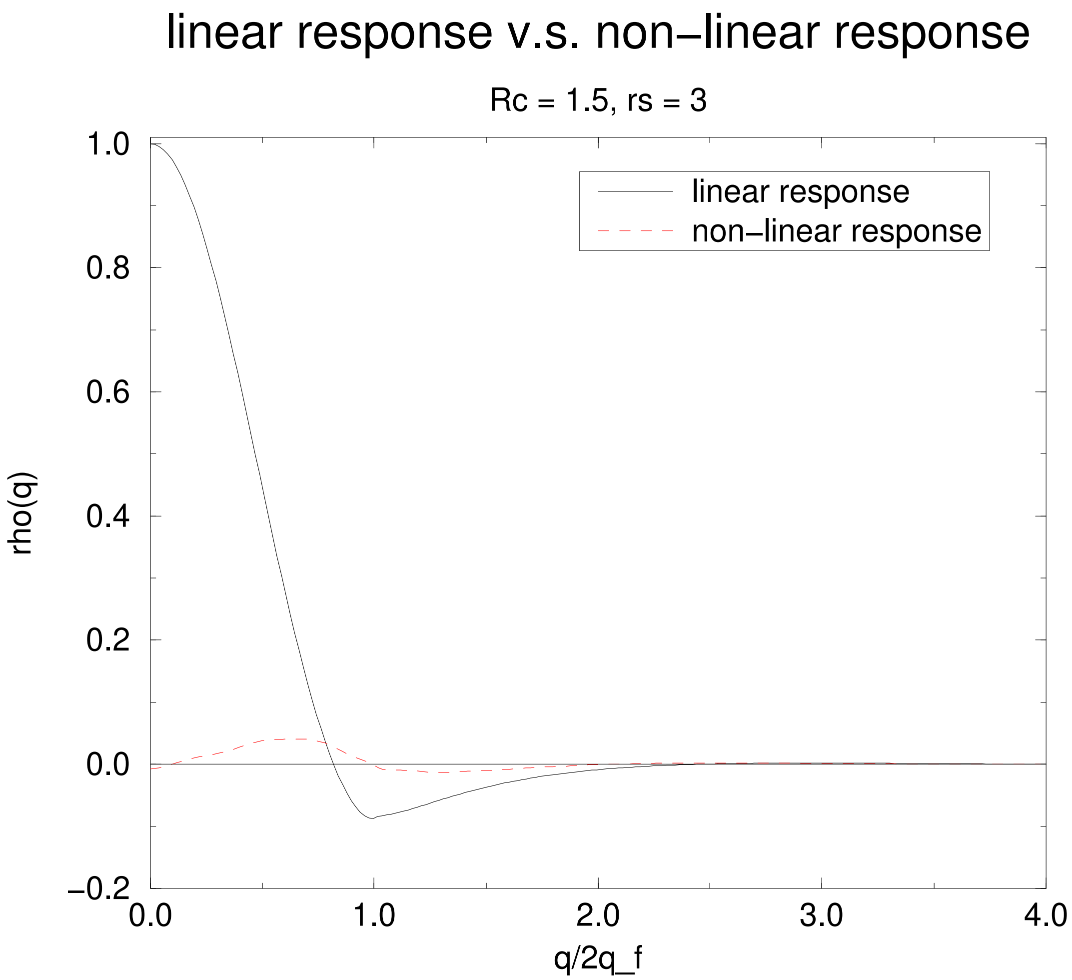

Figure 4.4: **Linear response compared to 2nd order response for $rs = 3$, $R_c = 1.5$, $Z = 1$.**
By plotting the linear response (which empirically captures the bulk of the full response) and the second-order response (which captures the bulk of what's left over) we obtain a sense of the scale of the first two orders in the expansion of equation 4.6.

Table 4.1: **Summary of the figures for fixing rs and varying R_c**

Figure	*electron density rs*	*APP cutoff parameter R_c*
figure (4.5)	$rs = 2$	$R_c = 0.0 \rightarrow 2.0$
figure (4.6)	$rs = 3$	$R_c = 0.0 \rightarrow 2.0$
figure (4.7)	$rs = 5$	$R_c = 0.0 \rightarrow 2.0$

2nd order response for q_0 v.s. $2k_F$

The first variation we investigate is the influence of R_c for a fixed rs; the parameters are listed in table 4.3.3. The degree of non-linear response increases as rs increases (and the density goes down). This can be understood at the level of Thomas-Fermi[5] theory; the second order Thomas-Fermi response is given by:

$$\chi_2^{TF}(k_1, k_2, k_3) = \frac{1}{6\pi^2 k_F} \tag{4.17}$$

which is independent of the arguments k_i and scales with rs, becoming more important at lower densities (higher rs). We expect that as R_c *increases* and the APP potential becomes weaker, the non-linear response *decreases*[6] A more careful look at figures 4.5 - 4.7 shows that things aren't quite so simple: Increasing R_c does not always imply decreasing response. Also, the functional form of the non-linear response varies depending on R_c. A look at the length-scales hints at a more illuminating way to plot the effect of the response: namely, first fixing $q_0/2k_F$ and then varying the electron density parameter rs. The parameters in the figures are summarized in table (4.3.3). The total response for a given $q_0/2k_F$ does always increase with increasing rs. Note how similar the functional forms are for a given

[5] Or Fermi-Thomas

[6] Keep in mind that the scale of the linear response is set by the perfect-screening sum-rule: $\rho_1(k = 0) = 1$ for all R_c and rs in this case.

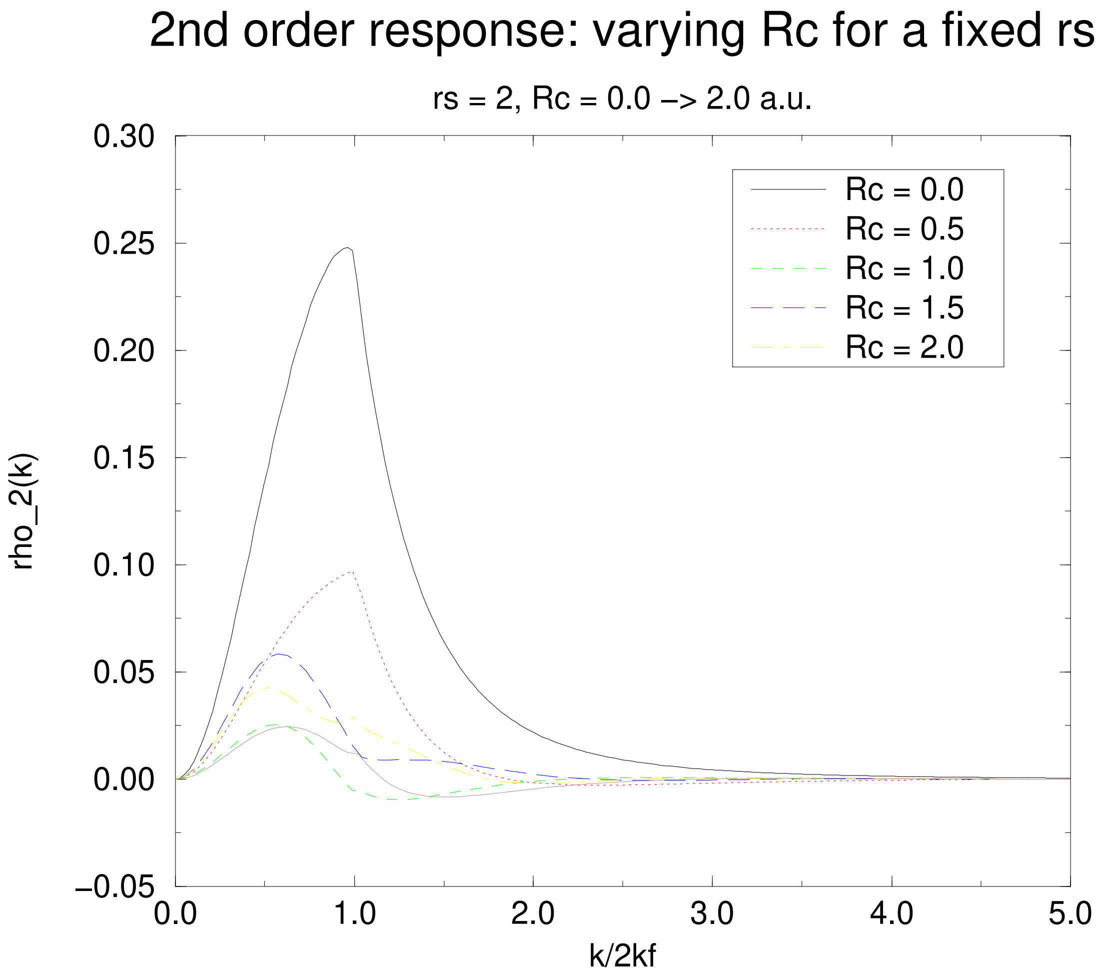

Figure 4.5: **2nd order response: varying R_c for a fixed $rs = 2$**
For a fixed rs, we vary R_c from 0.0 a.u. (Hydrogen) to 2.0 a.u. (equivalent to an ionization energy of about 0.36 Ry). In this case, $rs = 2$ is equivalent to a very high density (about that of aluminum)

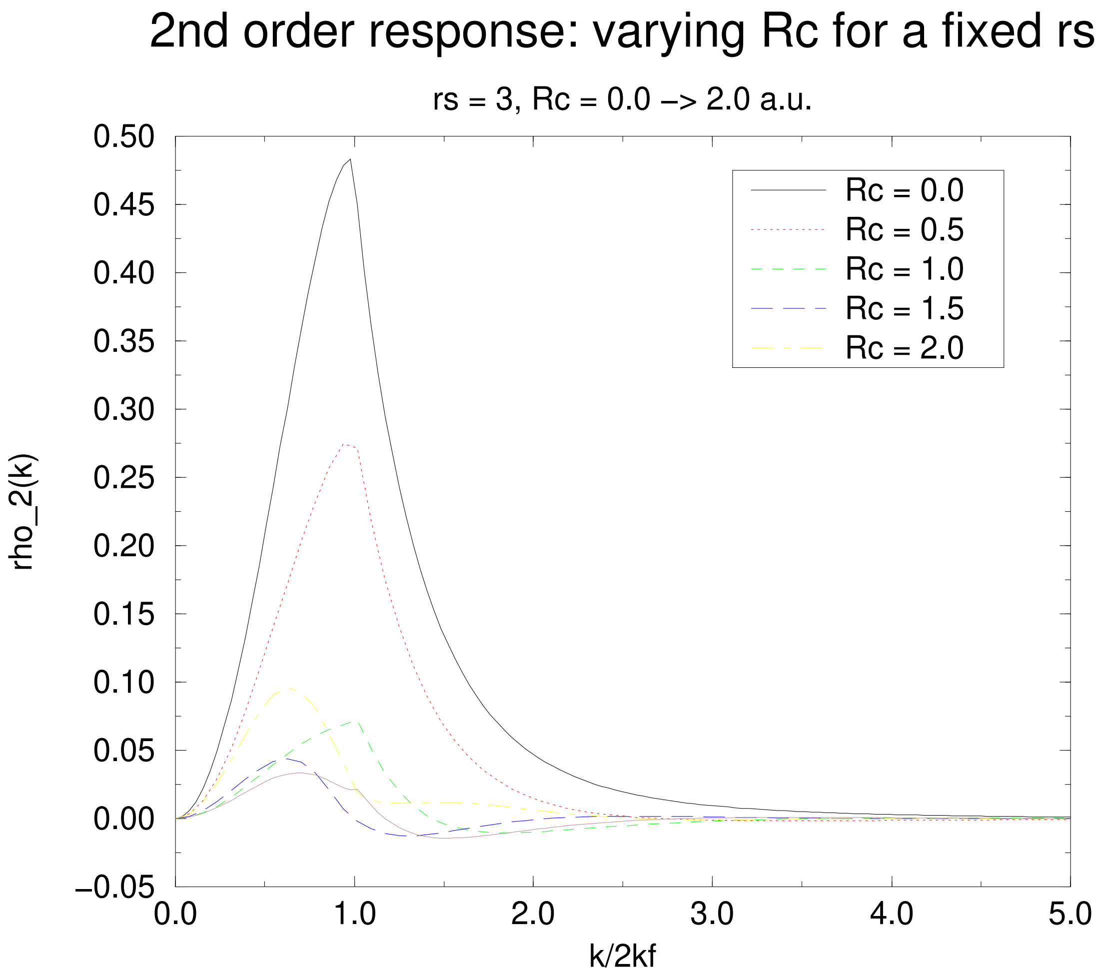

Figure 4.6: **2nd order response: varying R_c for a fixed $rs = 3$**
For a fixed rs, we vary R_c from 0.0 a.u. (Hydrogen) to 2.0 a.u. (equivalent to an ionization energy of about 0.36 Ry). In this case, $rs = 3$ is equivalent to a moderately high density (about that of silver or gold (materials that include d-electrons))

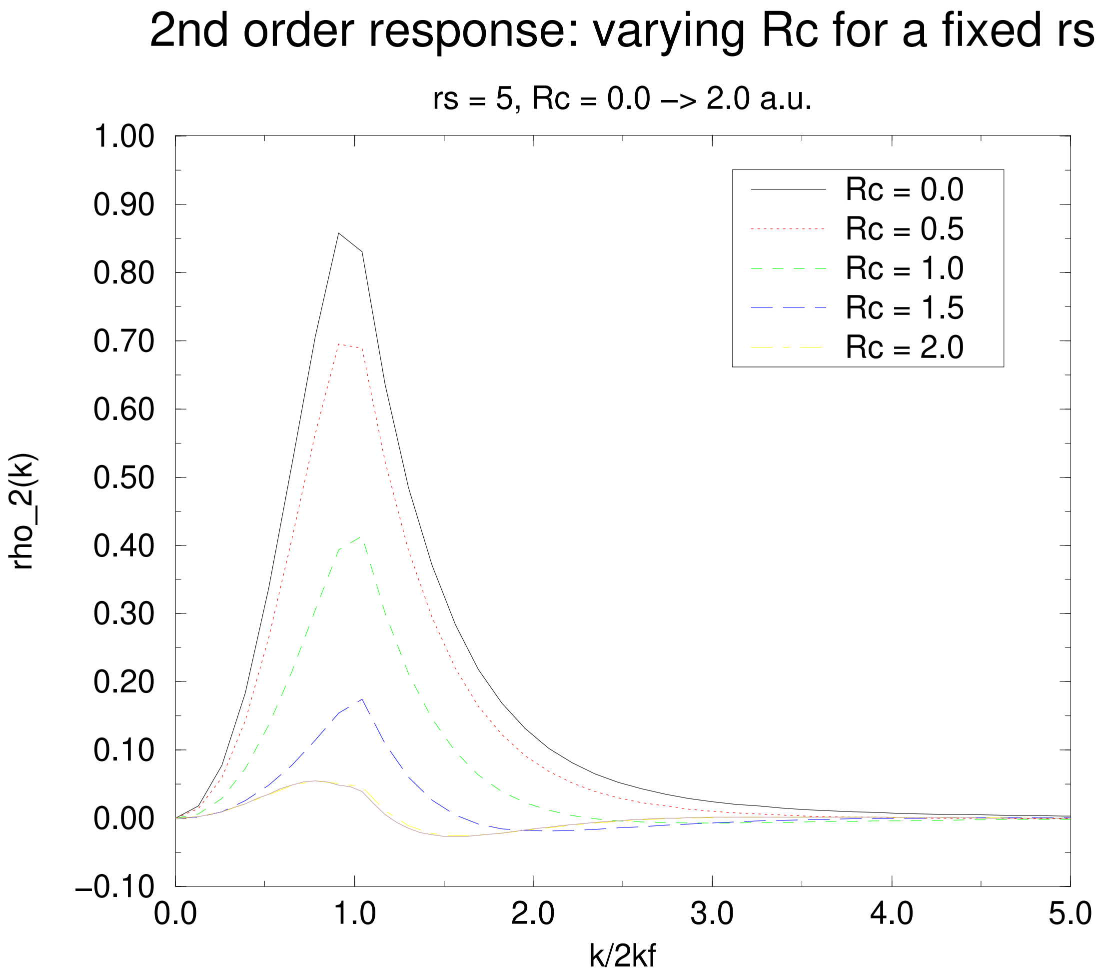

Figure 4.7: **2nd order response: varying R_c for a fixed $rs = 5$**
For a fixed rs, we vary R_c from 0.0 a.u. (Hydrogen) to 2.0 a.u. (equivalent to an ionization energy of about 0.36 Ry). In this case, $rs = 5$ is equivalent to a relatively low density (about that of potassium)

Table 4.2: **Summary of the figures for fixing $q_0/2k_F$ and varying rs**

Figure	*length-scale ratio* $q_0/2k_F$	*electron density* r_s
figure (4.8)	$q_0/2k_F = 0.5$	$rs = 1 \to 5$
figure (4.9)	$q_0/2k_F = 0.75$	$rs = 1 \to 5$
figure (4.10)	$q_0/2k_F = 0.9$	$rs = 1 \to 5$
figure (4.11)	$q_0/2k_F = 1$	$rs = 1 \to 5$
figure (4.12)	$q_0/2k_F = 1.25$	$rs = 1 \to 5$
figure (4.13)	$q_0/2k_F = 1.5$	$rs = 1 \to 5$
figure (4.14)	$q_0/2k_F = 2$	$rs = 1 \to 5$
figure (4.15)	$q_0/2k_F = \infty$ (hydrogen)	$rs = 1 \to 5$

$q_0/2k_F$. Among other things, the dielectric function $\epsilon(k)$ and the correlation parts of the local field corrections spoil the almost perfect scaling with rs.

Higher order response for hydrogen: $q_0 = \infty$

Hydrogen is an extreme limiting case of the Ashcroft empty-core pseudo-potential. There are no core-electrons and therefore no softening of the potential into a pseudo-potential. In fact, the lack of a core region produces qualitatively different behavior. For example the so-called "cusp-theorem"[14, 15, 16] implies that the induced density drops off as $\rho(k) \sim 1/k^4$ for large k[17]. Thus hydrogen is a worst-case scenario; the non-linear response is particularly strong. In fact, for a single proton potential in an electron gas, bound states set in for $rs > 1.7274$ and the linear response formalism is ill-defined [For more on this see the section on bound states].

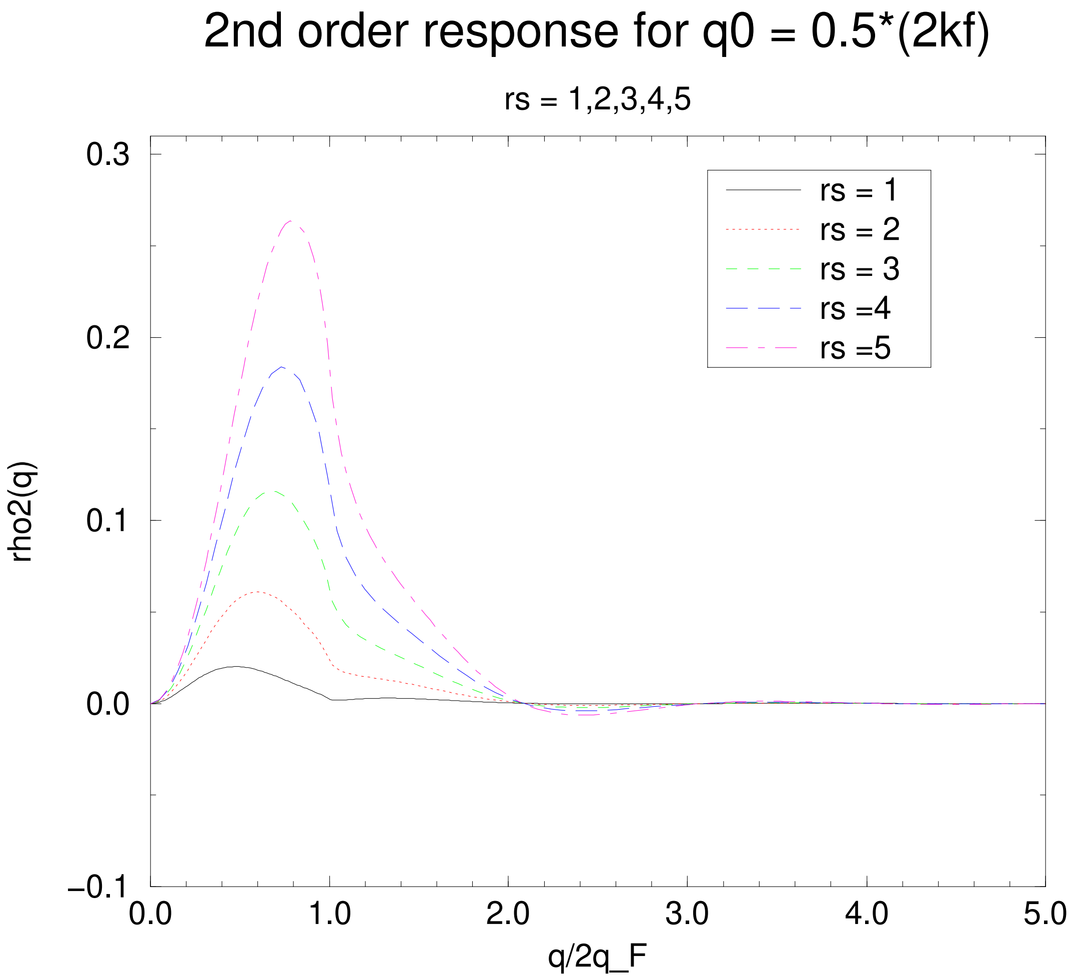

Figure 4.8: **2nd order response for** $q_0/2k_F = 0.5$; $rs = 1..5$
For $rs = 1..5$ we plot the second order response for $q_0/2k_F = 0.5$. Note how the functional form appears nearly the same, just scaled in the y-direction by a factor which increases with increasing rs

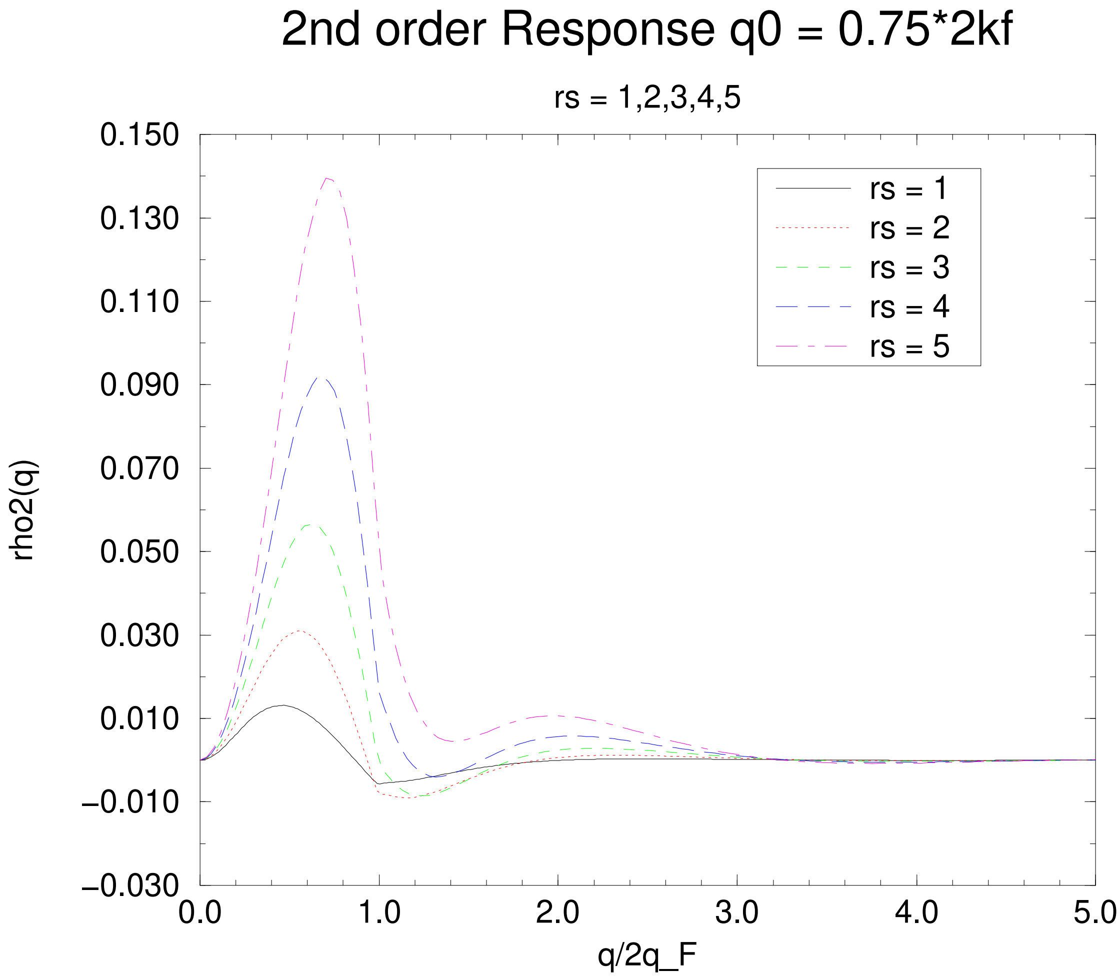

Figure 4.9: **2nd order response for $q_0/2k_F = 0.75$; $rs = 1..5$**
Same as figure 4.8, but with $q_0/2k_F = 0.75$

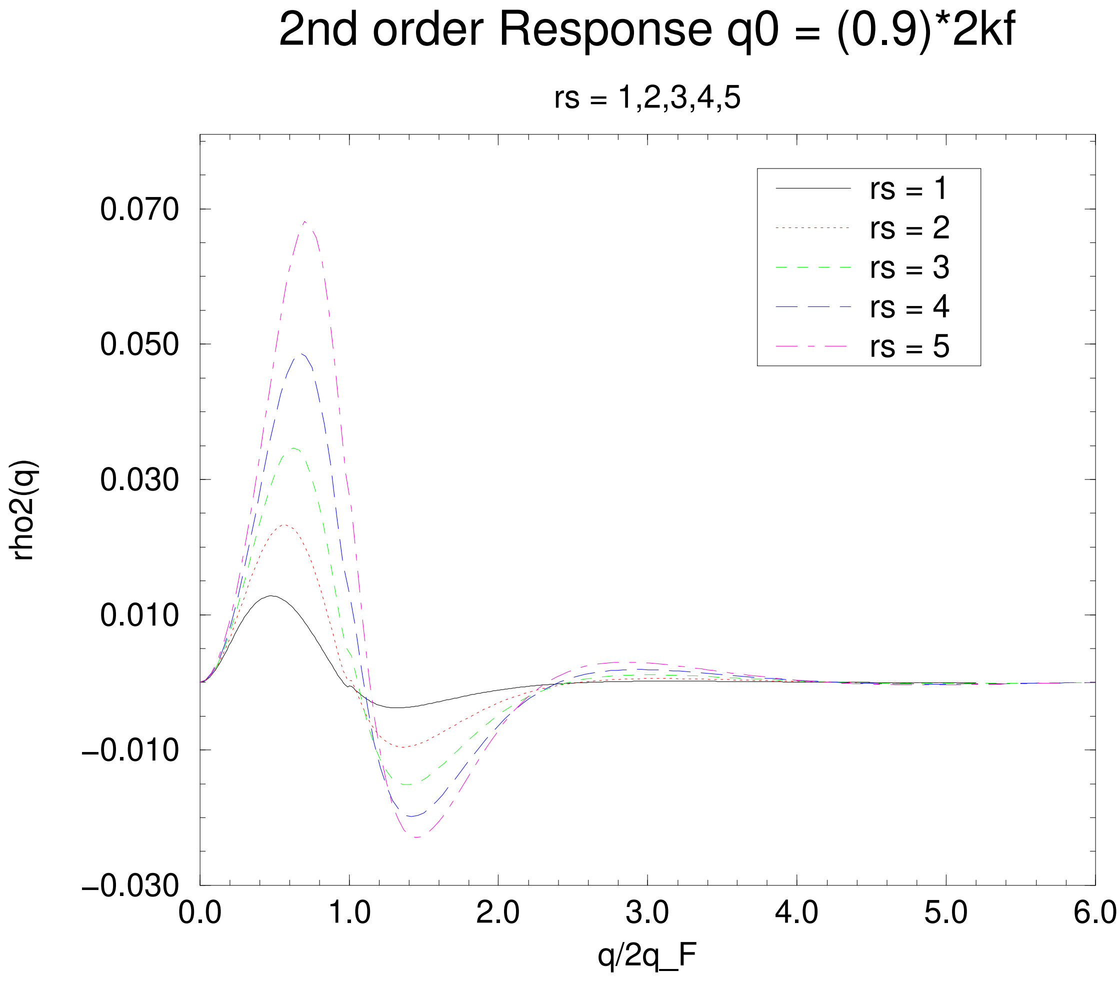

Figure 4.10: **2nd order response for** $q_0/2k_F = 0.9$**;** $rs = 1..5$
Same as figure 4.8, but with $q_0/2k_F = 0.9$

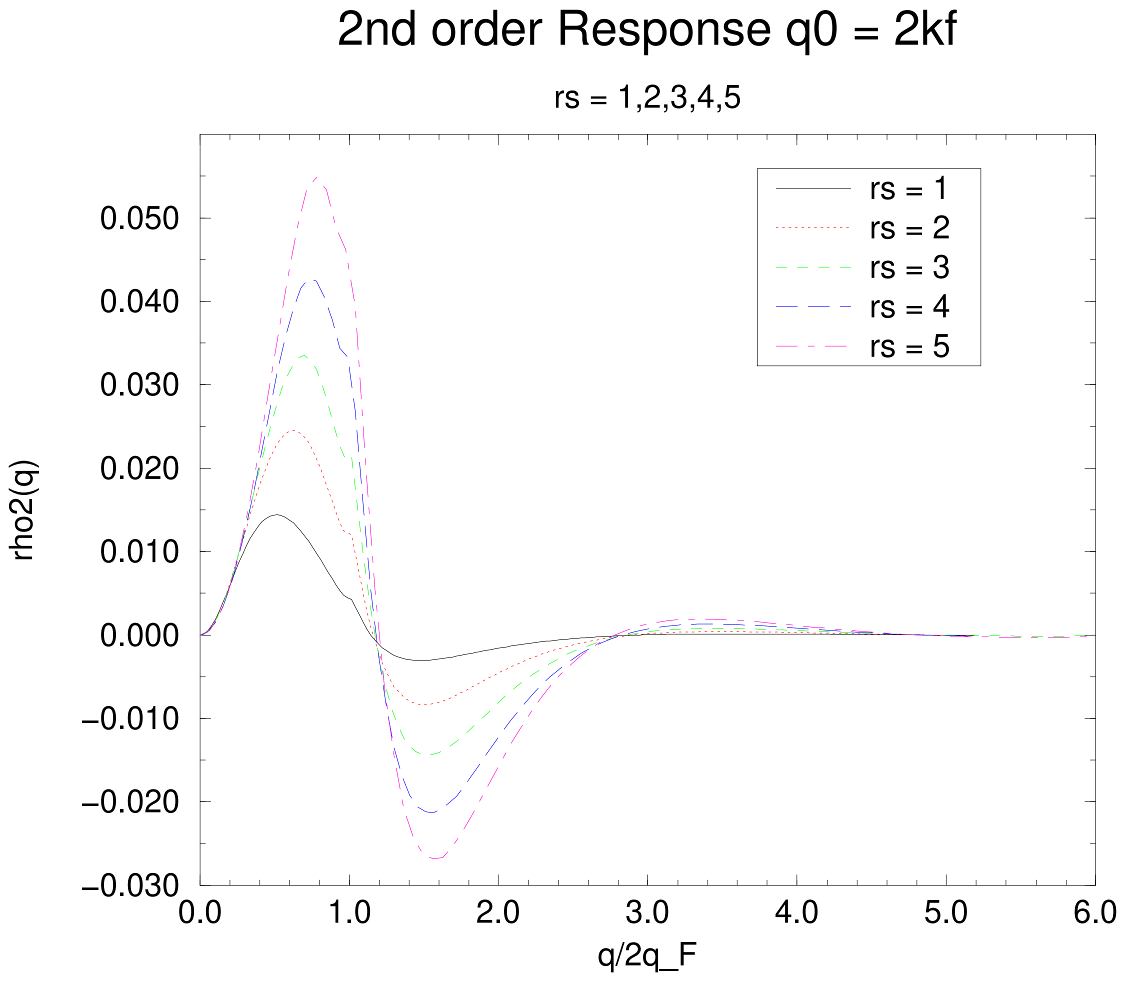

Figure 4.11: **2nd order response for $q_0 = 2k_F$; $rs = 1..5$**
Same as figure 4.8, but with $q_0/2k_F = 1$ Note how small the response has become.

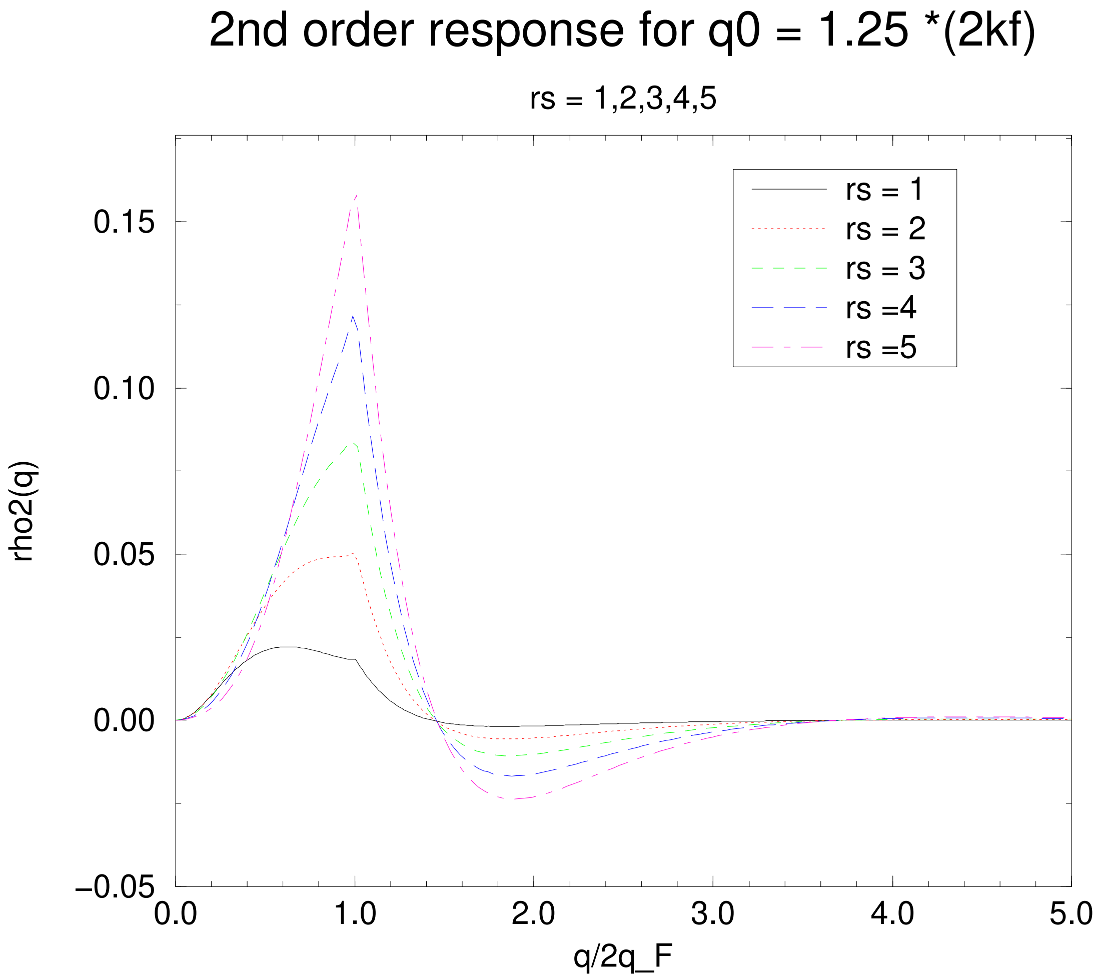

Figure 4.12: **2nd order response for** $q_0/2k_F = 1.25$; $rs = 1..5$
Same as figure 4.8, but with $q_0/2k_F = 1.25$ Note the similarity in scale (but difference in shape) with $q_0/2k_F = 0.75$.

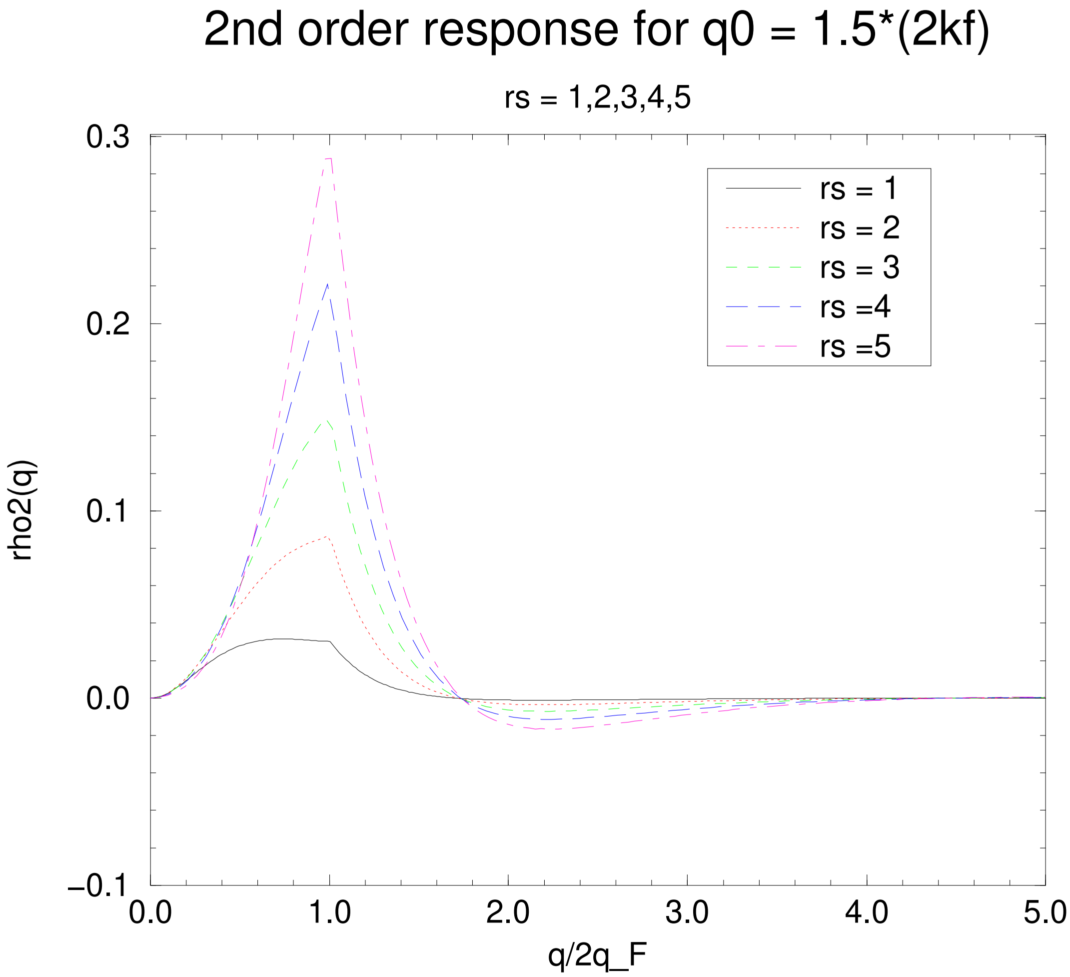

Figure 4.13: **2nd order response for** $q_0/2k_F = 1.5$**;** $rs = 1..5$
Same as figure 4.8, but with $q_0/2k_F = 1.5$

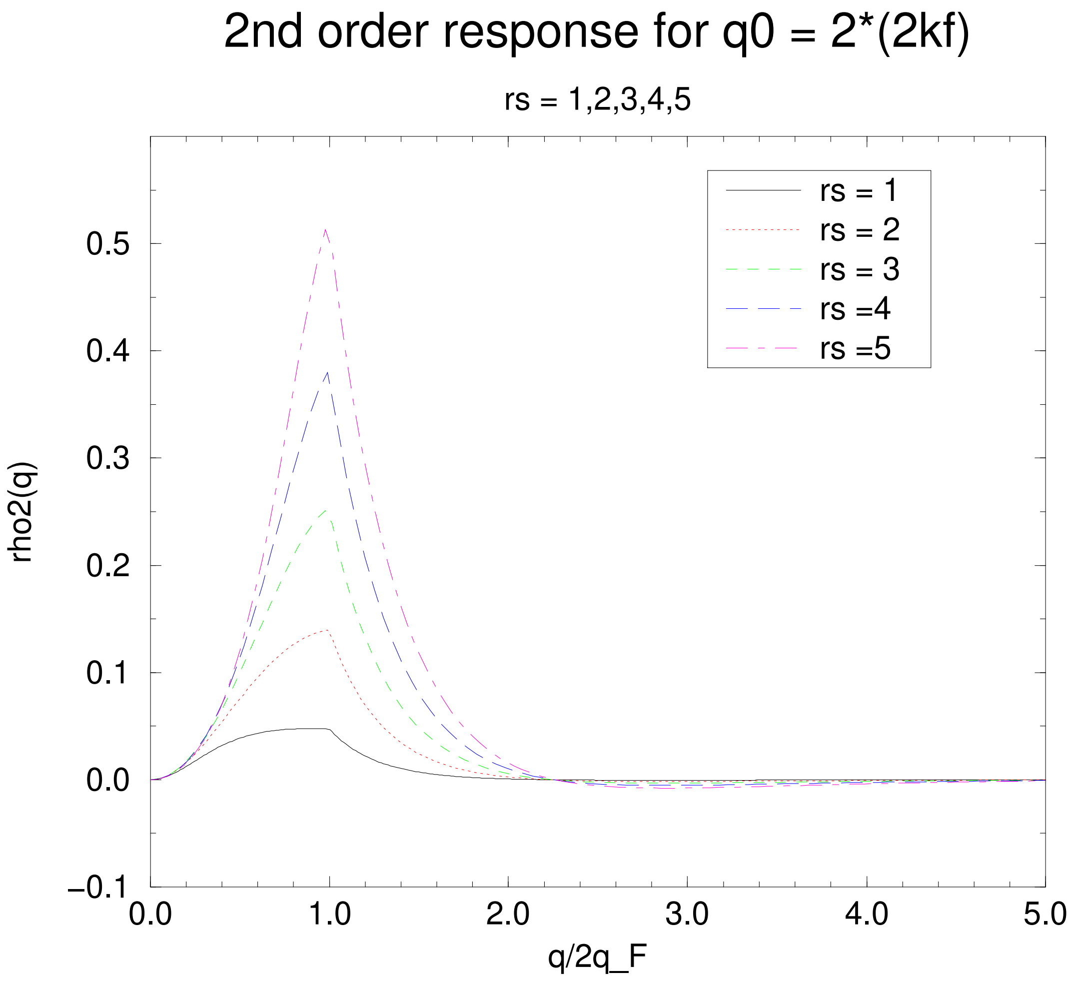

Figure 4.14: **2nd order response for $q_0/2k_F = 2.0$; $rs = 1..5$**
Same as figure 4.8, but with $q_0/2k_F = 0.75$ Larger q_0 implies smaller R_c and concomitant larger 2nd order response.

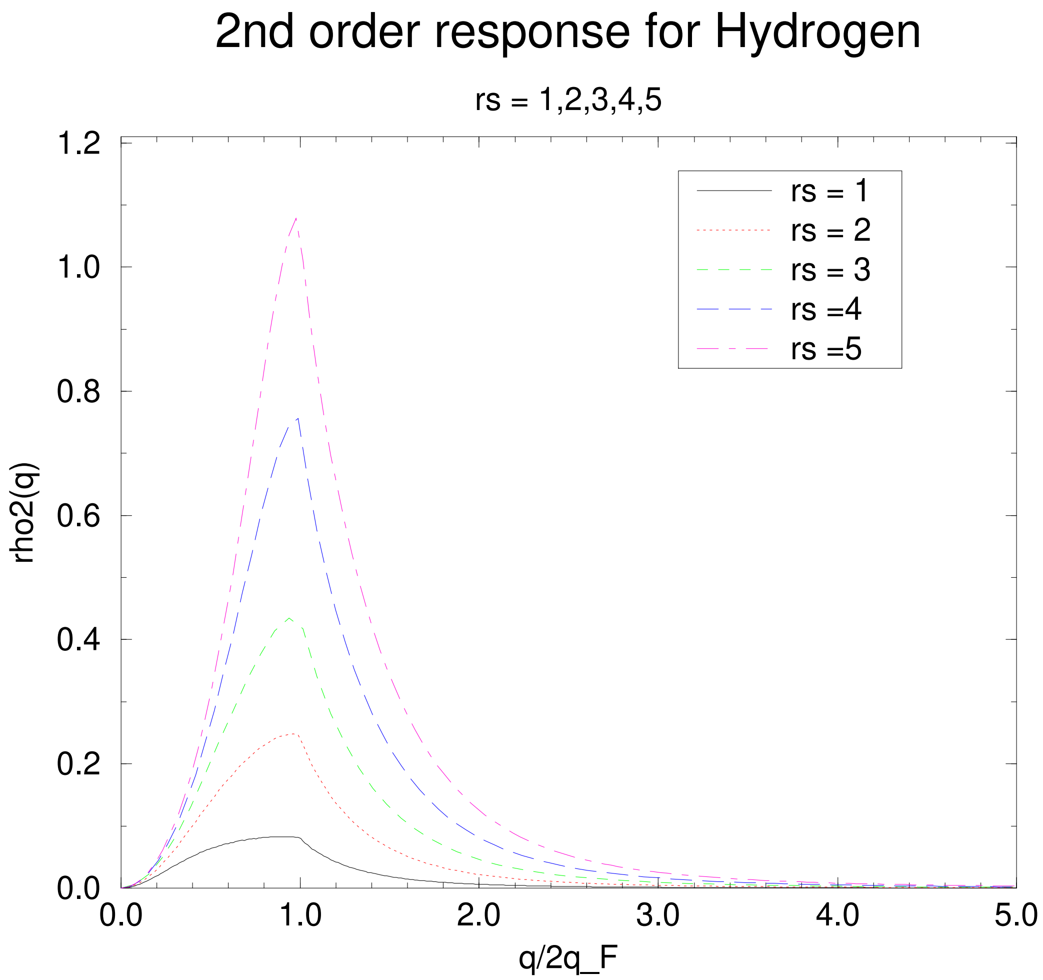

Figure 4.15: **2nd order response for $q_0/2k_F = \infty$ (i.e. hydrogen) ; $rs = 1..5$** For hydrogen we plot the second order response for $rs = 1..5$ Note how the functional form appears nearly the same, just scaled in the y-direction by a factor which increases with increasing rs. Note also how large the 2nd order response is compared to the APP of the previous figures.

The second minimum at $q_0 = 2k_F$

A look at the preceding figures shows a remarkable decrease in the 2nd order response, with a minimum at $q_0 = 2k_F$. This is depicted in figure 4.16 where the maximum of the second order response is used as a measure of the total second order response for $rs = 3$ (the same picture holds for other rs as can easily be seen by comparing figures 4.8 - 4.14). Apparently, when $q_0 \sim 2k_F$, there is a local minimum in the scale of second order response. We attribute this minimum to the following physical effect: The second order response function $\chi_2(k, k_1, k_2)$, peaks when the summed arguments in (4.14) are near $2k_F$. If the pseudo-potential zero-crossing q_0 is at the response peaks at $2k_F$, a maximum cancellation or *destructive interference of the atomic and electronic lengthscales* occurs, leading to a minimum in second order response. We postulate that a similar interference effect occurs for higher order terms in the series (4.14). At normal equilibrium conditions, most metals have an atomic R_c parameter and an electron density rs parameter such that the ratio $q_0/2k_F$ varies between about 0.75 and 1, very near the minimum in non-linear response. At present we know of no physical reason why this should be linked to a minimum of the second order response. The ratio of the atomic and electronic length scales is set by simply assembling N empty-core pseudo-potentials with a given R_c together with the requisite number of electrons and letting the system come to equilibrium with its surroundings. Girifalco[18] has even taken the experimental rs parameters together with a simple formulation of the energy (neglecting pair and higher order terms which only contribute a few % to the energy anyway) and by setting the pressure ($p = -(\partial E/\partial V)$) to zero, he obtained a very reasonable set of R_c parameters, demonstrating that the ratio is set almost completely by volume energy terms and is almost independent of structure and 1st or 2nd order response[20]. Thus at present it appears that the minimum in higher order response may be a fortuitous situation. but in retrospect the presence of this minimum may help explain why the ever popular linear response formulations of materials have been so successful. We note that historically, the NFE approximation has often been justified in a more general context than linear response alone by appealing to the fact that for a crystalline solid, the reciprocal lattice vectors are typically near the pseudo-potential zero-crossing q_0 so that the scattering is small[2].

4.3.4 The effect of local field factors

For comparison with the LDA infinite order response we needed the LDA local field factors, easily derivable as derivatives of the known LDA exchange correlation potential. The question immediately arises: What are the effects of exchange and correlation on this induced density? To answer this we plot the second order density without μ_1 or without μ_2 or without both (the latter is equivalent to the random phase approximation (RPA)[2]). The figures are summarized in table (4.3.4)[7]. Note how the two orders of exchange correlation effects cancel each other out at second order.

4.3.5 The role of bound-states

In Mott's seminal 1949 paper[21] he demonstrated how the screening of a Coulomb potential in an electron gas would, with increasing electron density, lead to the disappearance of the bound state and thus eventually to metallic behavior for an array of such potentials. If the Thomas-Fermi screening is applied the potential

[7] Note the slight change in notation, in the the exchange correlation factors μ_i are denoted by $G_i(..) = (8\pi/q^2)\mu_i$.

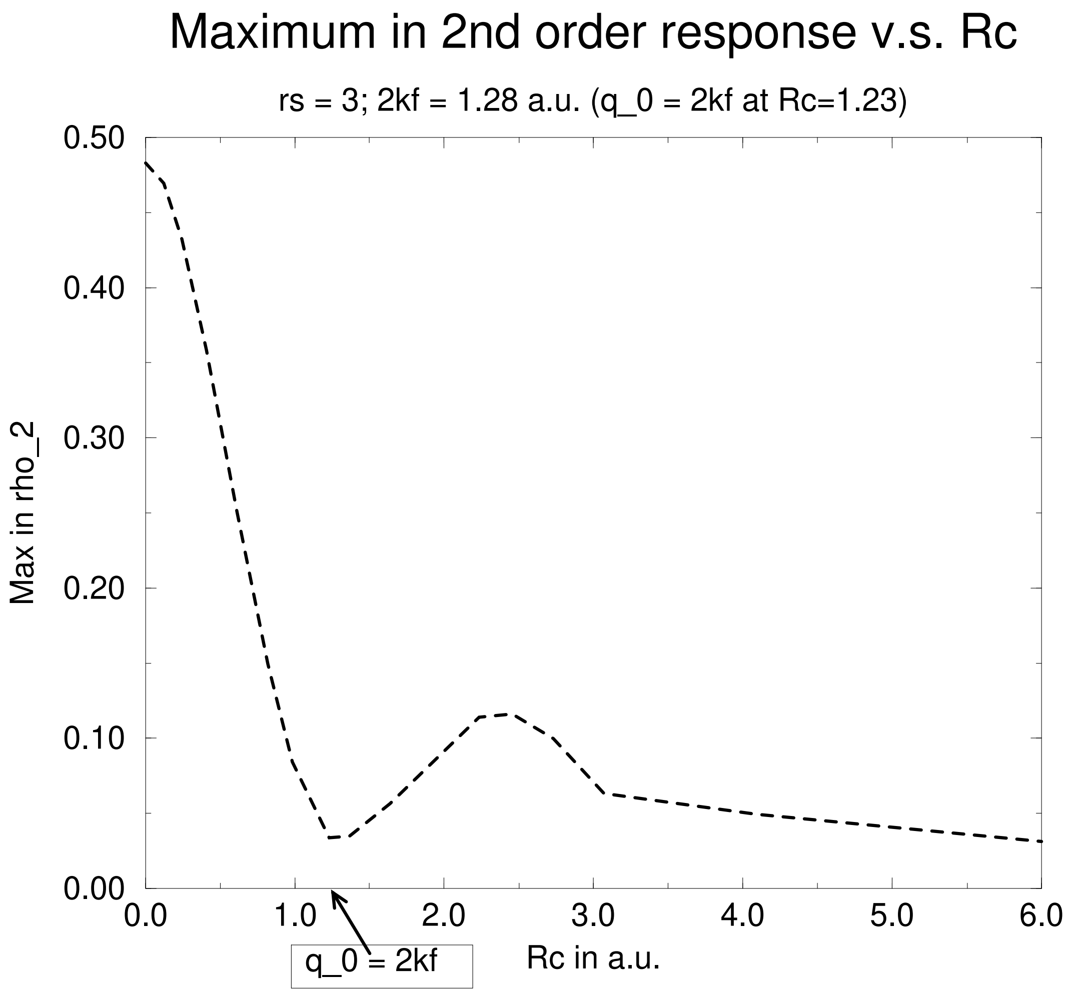

Figure 4.16: **Maximum in 2nd order response for $rs = 3$ as a function of R_c** We plot the maximum in second order response as a function of R_c for $rs = 3$. As expected, the response is largest for $R_c = 0$, or hydrogen, but note the secondary minimum at $q_0 = 2k_F$. It is about a factor 3 smaller than the secondary maximum at $\sim q_0/2k_F = 0.5$. This minimum in the higher-order response occurs near the normal equilibrium conditions of most metals; the exception being hydrogen.

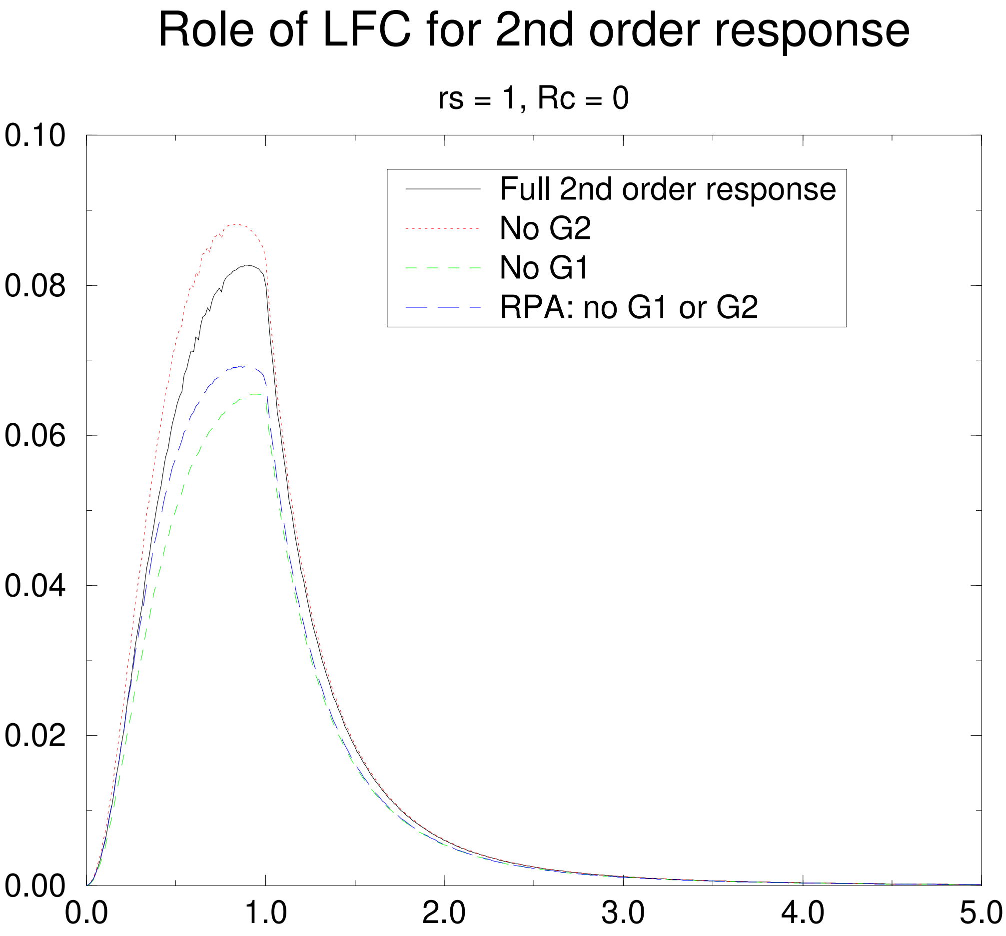

Figure 4.17: **Effect of local field corrections on response:** $rs = 1$, $R_c = 0$ **(hydrogen)**
Note how the effects of the 1st and 2nd order local field factors (called G1 and G2 here) partially cancel each other out.

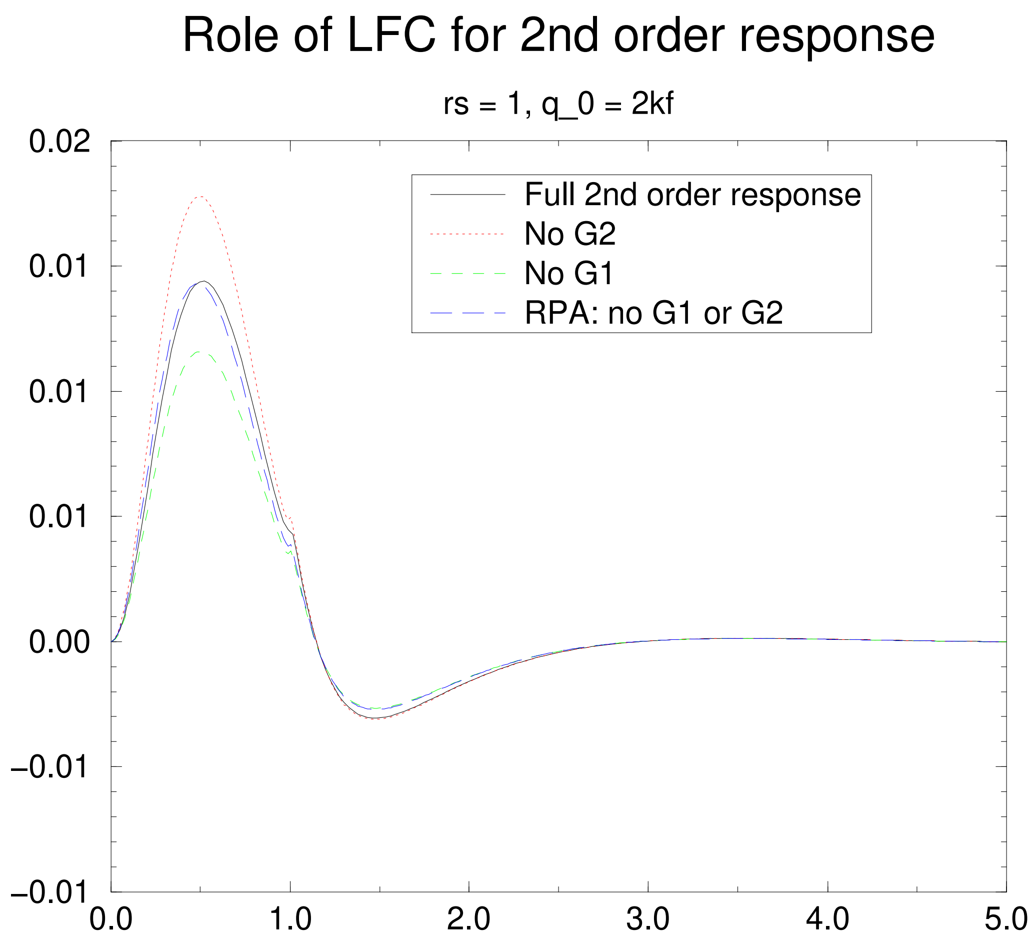

Figure 4.18: **Effect of local field corrections on response:** $rs = 1$, $q_0 = 2kf$ Here the effects of the 1st and 2nd order local field factors (called G1 and G2 here) almost exactly cancel each other out.

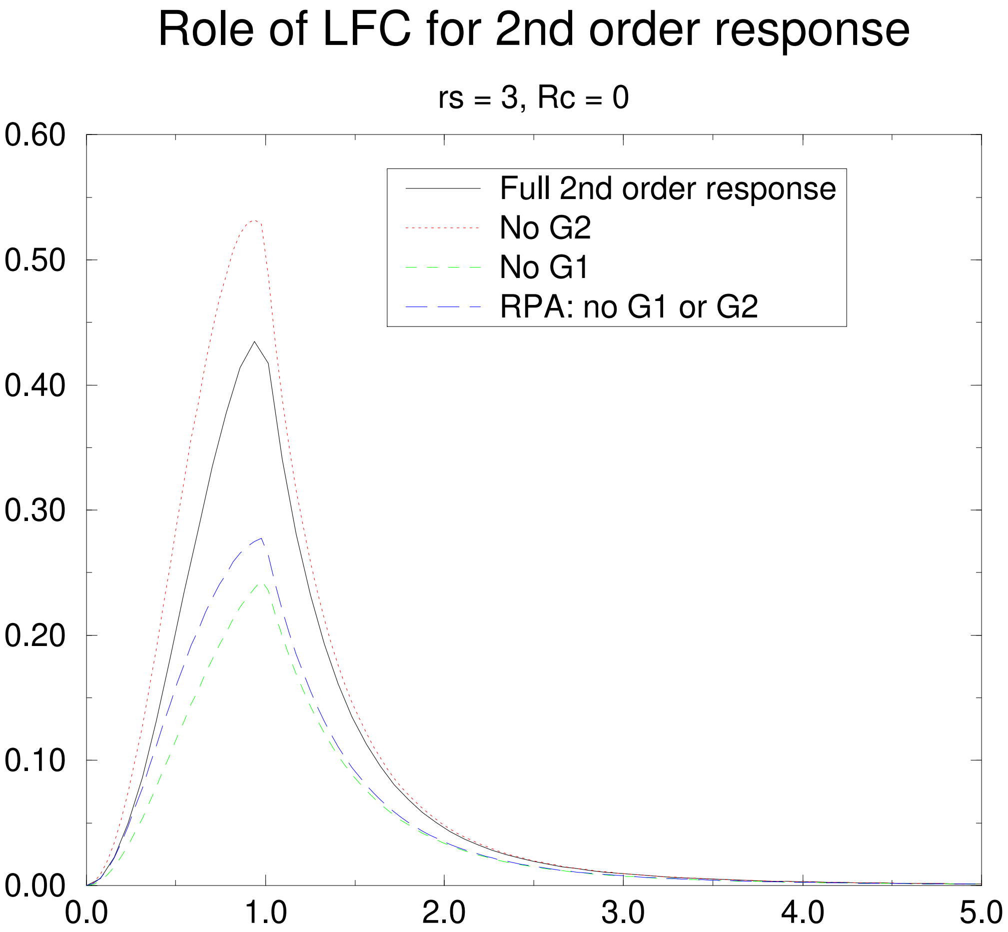

Figure 4.19: **Effect of local field corrections on response: $rs = 3$, $R_c = 0$ (hydrogen)**
Note that technically we are in the bound-state regime here; the response formalism is ill-defined.

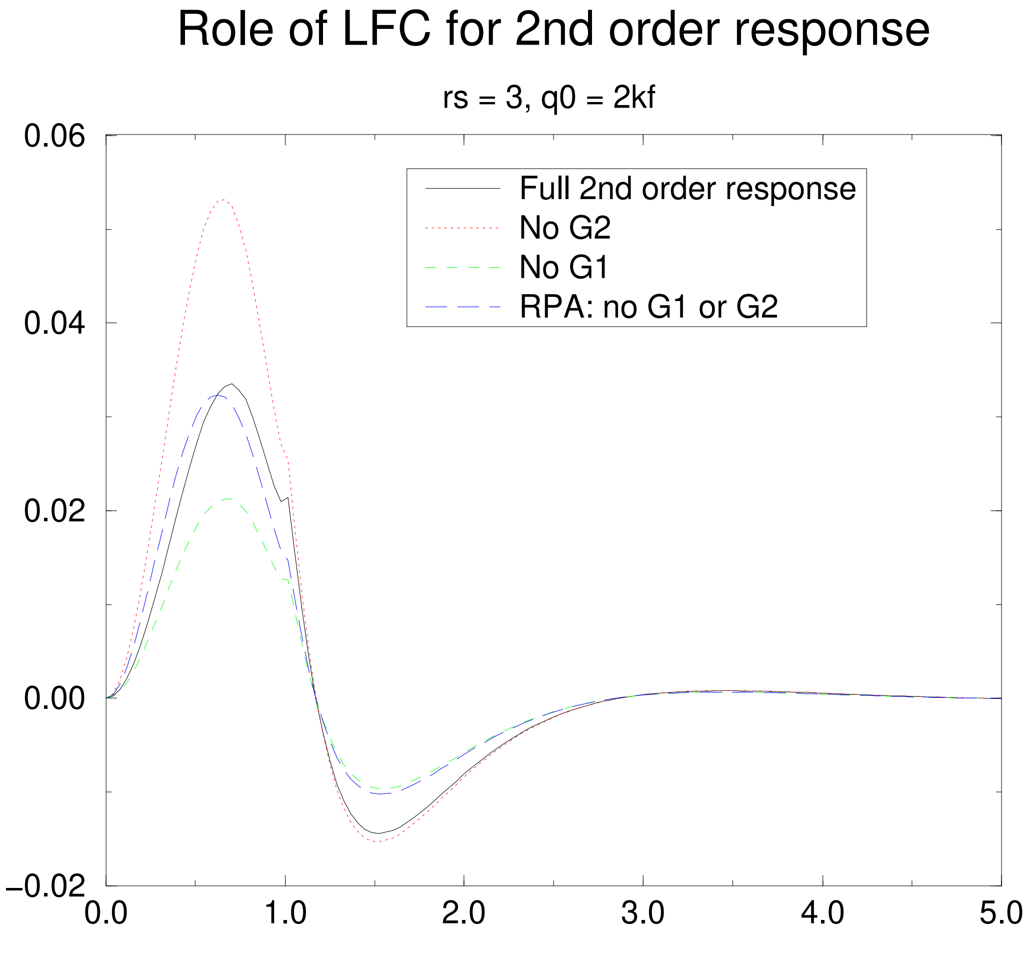

Figure 4.20: **Effect of local field corrections on response:** $rs = 3$, $q_0 = 2k_F$

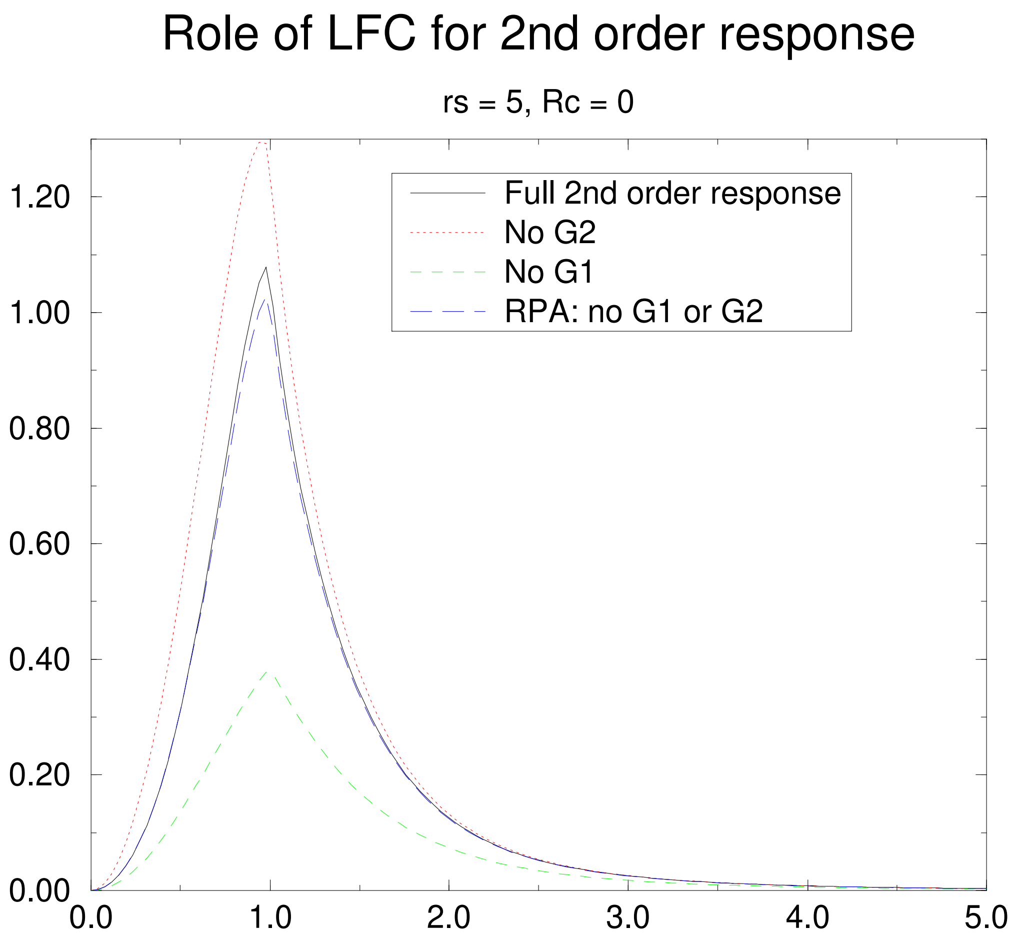

Figure 4.21: **Effect of local field corrections on response:** $rs = 5$, $R_c = 0$ **(hydrogen)**
Again, note that technically we are in the bound-state regime here; the response formalism is ill-defined.

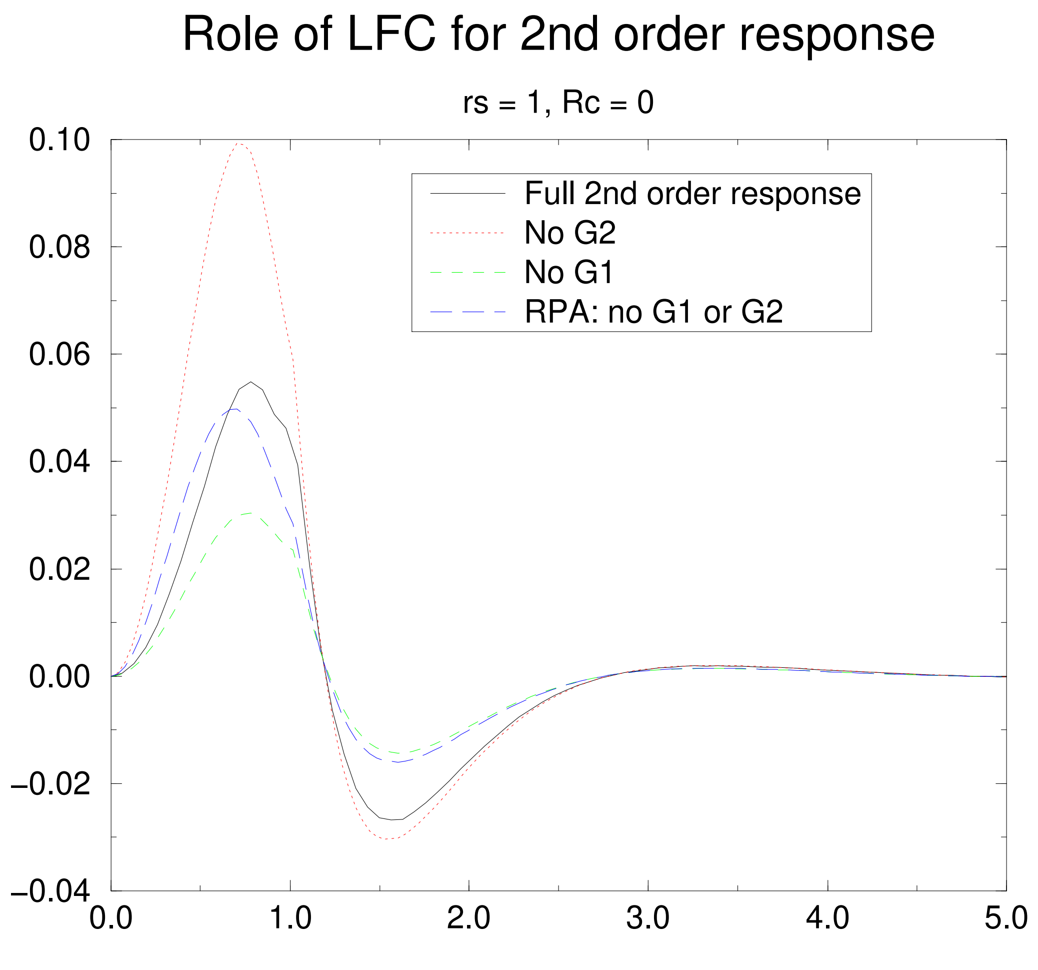

Figure 4.22: **Effect of local field corrections on response:** $rs = 5$, $q_0 = 2k_F$

Table 4.3: **Summary of the figures for fixing $q_0/2k_F$ and varying the local field factors G_i.**

Figure	*length-scale ratio* $q_0/2k_F$	*electron density* r_s
figure (4.17)	$q_0/2k_F = \infty$ (hydrogen)	$rs = 1$
figure (4.18)	$q_0/2k_F = 1$	$rs = 1$
figure (4.19)	$q_0/2k_F = \infty$ (hydrogen)	$rs = 3$
figure (4.20)	$q_0/2k_F = 1$	$rs = 3$
figure (4.21)	$q_0/2k_F = \infty$ (hydrogen)	$rs = 5$
figure (4.22)	$q_0/2k_F = 1$	$rs = 5$

becomes:

$$v(r) = \frac{-2Z}{r} e^{-q_{TF} r}, \tag{4.18}$$

where q_{TF} is the inverse screening length given by[22]:

$$q_{TF} = 0.815 k_F \, (rs)^{1/2} \tag{4.19}$$

in atomic units. According to Mott, the bound-state disappears roughly when;

$$q_{TF} a_H^* \sim 1, \tag{4.20}$$

where a_H^* is the effective Bohr radius (which we'll take to be a_0 (=1 in atomic units)). From this he derived his famous scaling law for doped semi-conductor metal-insulator transitions[23]. Later more accurate analytical and numerical calculations[24, 25] gave a critical q_{TF} of:

$$q_{TF}^* = \left(\frac{0.83991}{Z}\right)^{-1}, \tag{4.21}$$

so that the critical electron density parameter rs^* at which bound-states disappear for a Coulombic potential with Thomas-Fermi screening is:

$$rs^* = \frac{1.7274}{Z^2}. \tag{4.22}$$

For an APP screened in the same manner, the critical rs^* still scales in roughly the same with Z and is an increasing function of R_c. For example when $Z = 1$, the $rs^*(R_c = 1) \sim 3.7$ and $rs^*(R_c = 1.5) \sim 4.4$. The response formulation is derived from a plane-wave basis set and breaks down when bound-states are involved[26], while the LDA program we use takes the bound states into account. Thus direct comparisons between the two approaches are strictly correct only for rs less than the critical rs^*. However, in a real physical system, the ions are not isolated. Instead multiple ions combine to form an electron band, lowering the ionization threshold, and increasing considerably the rs^* for a given R_c. Response theory without bound states may be physically valid to higher values of rs than one would naively expect based on the criterion above. In fact, the atom-in-jellium calculations form an important input for effective medium theories[12] of metallic bonding, and some care as to the effect of these (physically spurious) bound states should probably be taken into consideration. As an example of their effect, we show in figure 4.23 the full response minus linear response that was so well approximated by the 2nd order response for the case of no bound states (see for example figure 4.3). Note how the bound-state gives an opposite sign for LDA non-linear response from the 2nd order response[8]

As a caveat to the arguments above, we add that although for systems like

[8] This difference is not due to the the potential being too strong for a convergent response summation. At small q the non-linear response goes as q^2 with an easily calculable positive pre-factor.

aluminum, the single pseudo-potential has bound-states while the physical system, with many potentials together, is metallic (i.e. no bound states), the opposite is true of hydrogen. At the critical density of $rs^* = 1.7274$ the physical system with many potentials together is still well within the (diatomic) insulating regime.

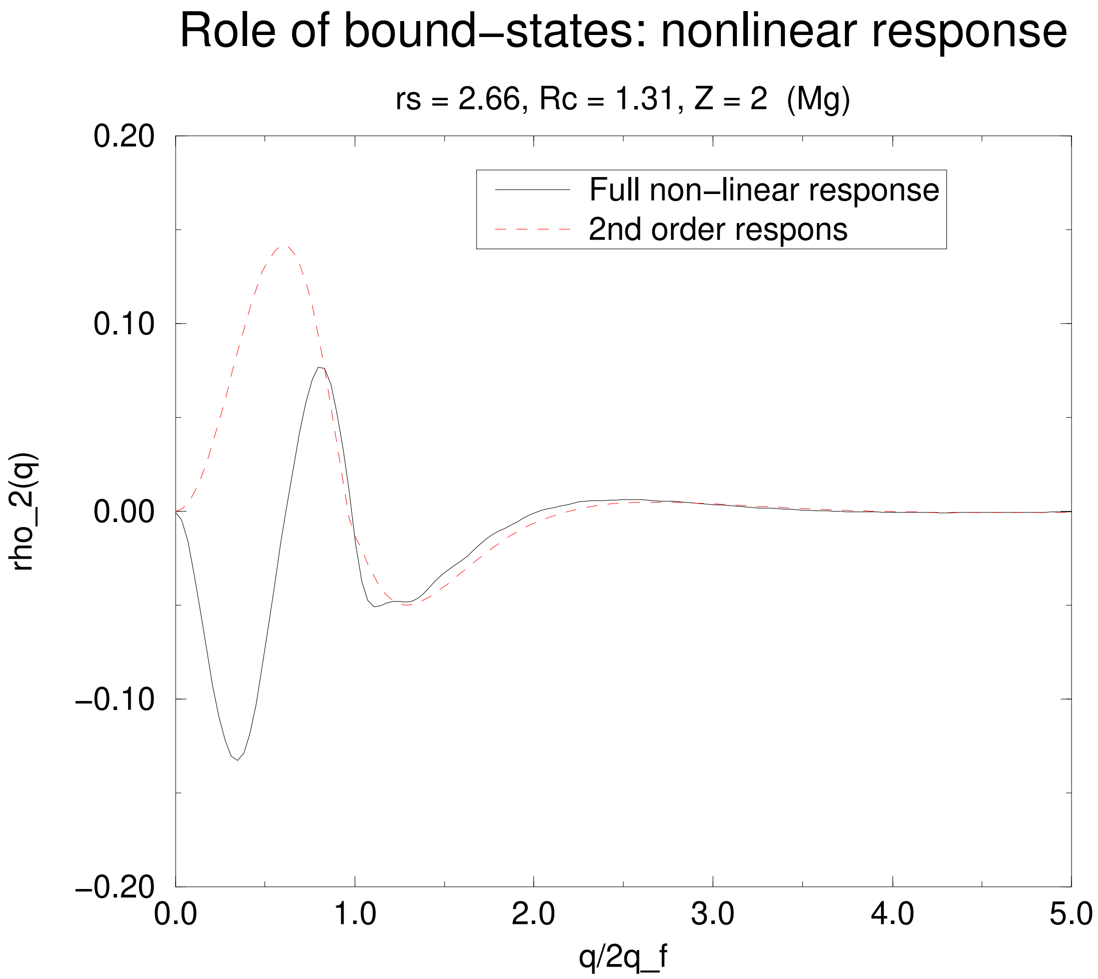

Figure 4.23: **Non-linear response with a bound state compared to 2nd order response theory.**
The single $Z = 2$ potential with parameters for Magnesium has a bound-state and as a consequence, response theory breaks down.

4.4 Final Discussion and Conclusions

In conclusion we have shown why linear response works remarkably well and captures the dominant structure of the density induced by an external pseudo-potential. One could imagine that this stems from higher terms that vary in sign and thus cancel between different orders, but, as depicted in figure 4.3, the second order term actually dominates the non-linear response and is itself small. Thus instead, it appears that each higher order term in the series is small (self cancellation within each term); the series converges very rapidly. This stems in part from an interference effect between the atomic length scale q_0 and the electronic length-scale $2k_F$. The glaring exception to all this is hydrogen. Because it has no core region and thus no interference effect to lower the higher order terms in the response series, the higher order terms are not small, the series may not even converge.

The ability of the second order term to capture the dominant part of the non-linear response allows us to explore the effects of exchange and correlation on non-linear response. One interesting result is that the exchange-correlation effects cancel each other between first and second order which implies that theories based on a linear response approximation only may over-estimate the effect of exchange and correlation. An important example of this would be effective ion-ion potentials derived from a linear response approximation. Hydrogen may be an important exception.

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[1] A great body of work on pseudo-potentials already exists. Currently the most popular are the so-called "Ab-Initio" pseudo-potentials used in plane-wave numerical techniques[2, 4] which require the density outside a given core radius to be identical to that of the full atom. If in addition the inner part is "norm-conserving", then the derivatives of the scattering phase shifts are also correct, so the new "pseudo-atom" can be more easily transferred to different condensed matter environments. Before the emergence of (non-local) Ab-Initio pseudo-potentials, various empirical forms were fit to some know experimental data (e.g. Fermi-surface properties etc...). For an extensive overview of that earlier work see for example M. Cohen and V. Heine in *Solid State Physics* **24** (1970).

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