Second-order perturbation theory as applied to impurities in the electron gas

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May 1996

Abstract

The present paper describes the initial stages of a larger investigation aimed at assessing the accuracy and utility of straight-forward perturbation theory as a tool in the calculation of the total energy of electronic systems. In the present work we have inserted point charges and impurities represented by pseudo-potentials into the homogeneous electron gas. The corresponding relaxation energies have been calculated to third order in perturbation theory and the results have been compared to those of infinite order calculations within the local-density approximation. In the case of the very strong perturbation represented by a point charge, we find that the third-order contribution typically reduces the error from linear response (second-order in the potential) by two thirds. Remaining errors of the order of 10% in the regime of metallic densities are still too large to make third-order perturbation theory a viable approach. The accuracy of the exchange-correlation part of the energy is found to suffer the most from a perturbative approach, and when this part of the energy is treated in a more accurate way, errors can be brought down to an adequate level of a few per cent. For the weak perturbations represented by pseudo-potentials the perturbative approach gives accurate results.

1. Introduction.

In recent work [1], we have shown that a straight-forward gradient expansion gives very accurate exchange energies in *s-p* bonded metallic systems. There is also no reason to believe that the same would not prove to be true of correlation energies once we are able to calculate these energies in a reliable way. Thus, these two parts of the total energy of a solid can be accurately obtained using a relatively simple method for which, *e.g*, periodicity is not a required prerequisite. Other parts of the total energy which also are relatively easy to deal with even in low-symmetry systems are the classical electron-electron interaction and the interaction with the nuclei. It would thus be a major advantage if also the remaining part of the energy, *i.e.*, the kinetic energy could be calculated without reference to symmetry. One could then relatively easily deal with, *e.g.*, impurity problems or with disordered systems. Other problems which might be facilitated by such an approach would be the calculation of phonon frequencies or of the dielectric response to external perturbations. Two methods come to mind which would serve such a purpose. One would be to use a gradient expansion for the kinetic energy, *i.e.*, an extended Thomas-Fermi approach. Previous experience has, however, shown that the accuracy of this method is far from adequate for our purposes. Another possibility is straight-forward perturbation theory. Going up to third order in the total energy, *i.e.*, to second-order response theory is quite feasible but, at fourth order, this method starts to become as cumbersome as infinite-order methods. The present work should be considered as the first in a series of investigations concerning the accuracy and utility of straight-forward perturbation theory. The quality of the perturbative results can be assessed by comparing them to those of infinite-order theories, *i.e.*, to methods based on a direct solution of the Schrödinger equation of the problem. Such comparisons should be carried out in different systems such as, *i.e.*, periodic metals or semiconductors or for cases with impurities in periodic solids.

In the present work we will limit ourselves to the study of impurities in the electron gas and we will go to third order in perturbation theory. We will start by considering the classical case of a point charge in the electron gas. This is really a very strong perturbation on the system and we will also discuss the insertion of weaker impurities represented by pseudo-potentials into the gas. The results range from moderately disappointing to encouraging. It is found that the exchange-correlation part of the energy is more severely affected by the use of perturbation theory and we suggest a hybrid method in which this part of the energy is treated with higher accuracy as compared to third-order perturbation theory. This method relies on inserting the particle density obtained from second-order response theory into, *e.g.*, the local-density expression for the exchange-correlation energy. In this way, errors are brought down to the level of 5%, thus making the perturbative approach a viable scheme for total-energy calculations.

The paper is organized as follows. In Section 2 we give the basic formulas for third-order perturbation theory as applied to inserting a localized potential into an otherwise homogeneous but interacting electron gas. In the present work, all electron-electron interactions are treated within the local-density approximation (LDA). In Section 2 we also present a new simpler method for applying third-order perturbation theory to single-center perturbations which relatively easily can be generalized to cases of non-local angular-momentum dependent pseudo-potentials. For the the theory associated with solving the problem to infinite order we refer to Ref. [2]. In Section 3 we present and discuss our results and, finally, in Section 4 we give a short summary and a brief outlook on future research.

2. Perturbation Theory.

2.1 Localized perturbations in the gas.

Consider the Kohn-Sham equation [4] of an interacting N-electron system without spin-orbit interaction:

$$\left(-\frac{1}{2}\nabla^2 + w + \int n\,v + v_{xc}\right)\varphi_i = e_i\,\varphi_i\,, \tag{1}$$

where v is the Coulomb interaction, w the external potential, v_{xc} the exchange-correlation potential, and n is the electronic density given by:

$$n = \sum_{i=1}^{N}\mid\varphi_i\mid^2\,. \tag{2}$$

We may view the effective Kohn-Sham potential, $V = w + v_{xc} + \int n\,v$, as the external potential of a system of non-interacting electrons having the same density n as the interacting system. In this way, the density change δn due to a change in the effective potential δV is obtained from the independent-particle response functions χ_0 and ϕ_0

$$\delta n = \chi_0\,\delta V + \frac{1}{2}\delta V\,\phi_0\,\delta V + \cdots\,, \tag{3}$$

where δV is given by

$$\delta V = \delta w + \int v\,\delta n + \int K_{xc}\,\delta n + \frac{1}{2}\int L_{xc}\,\delta n\,\delta n' + \cdots \tag{4}$$

Here K_{xc} and L_{xc} are, respectively, the second- and third-order functional derivatives with respect to density of the exchange-correlation energy [3, 5]. The same change δn can, of course, be viewed as a response to a change δw in the external potential of the interacting system, thus defining the interacting or 'full' response-functions χ and ϕ

$$\delta n = \chi\,\delta w + \frac{1}{2}\,\delta w\,\phi\,\delta w + \cdots \tag{5}$$

Obvious spatial dependencies and integration signs will here be suppressed to make the equations more compact, i.e., n and n' are short for $n(\mathbf{r})$ and $n(\mathbf{r}')$ and so on.

When the first-order change, $\delta V = \delta w + (K_{xc} + v)\,\chi\delta w$, in the potential V due to variations, δw, in the external potential, is inserted into Eq.(3), one can equate terms linear in δw to obtain

$$\chi = \chi_0 + \chi_0\,(v + K_{xc})\,\chi\,. \tag{6}$$

Consider now a system consisting of an electron gas with a density n alongside a fixed positive uniform background charge with the same density n_0 and a small localized external potential w. This means, of course, that n will differ appreciably from n_0 only over a finite part of space. The grand potential, Ω, of this system can be written as a functional of the electron density n and the external potential w:

$$\Omega[n,w] = T_0[n] + \int w\,(n-n_0) + \frac{1}{2}\int(n-n_0)\,v\,(n'-n_0) + E_{xc}[n] - \mu\int(n-n_0)\,, \tag{7}$$

where the first, second, and third part of the equation above represent, respectively, the non-interacting kinetic-energy functional, the energy associated with the external

potential w, and the classical electrostatic energy. The fourth part is the exchange-correlation energy. Finally, μ is the chemical potential.

Let us then expand $\Omega[n, w]$ around $\Omega_0 = \Omega[n_0, 0]$ to third order in arbitrary changes in the potential and the density:

$$
\begin{aligned}
\Omega[n, w] &= \Omega_0 + \int \frac{\delta\Omega}{\delta n}\, \delta n + \int \frac{\delta\Omega}{\delta w}\, \delta w + \frac{1}{2} \int \frac{\delta^2\Omega}{\delta n\, \delta n'}\, \delta n\, \delta n' + \\
&\quad \int \frac{\delta^2\Omega}{\delta w\, \delta n} \delta n\, \delta w + \frac{1}{6} \int \frac{\delta^3\Omega}{\delta n\, \delta n'\, \delta n''}\, \delta n\, \delta n'\, \delta n''\,,
\end{aligned} \tag{8}
$$

From Eq.(7) we then obtain:

$$
\begin{aligned}
\Omega[n, w] &= \Omega_0 + \int \Big(\frac{\delta T_0}{\delta n} + v_{xc} - \mu\Big)\, \delta n\ + \int \delta w\, \delta n\ + \\
&\quad \frac{1}{2} \int \Big(\frac{\delta^2 T_0}{\delta n \delta n'} + v + K_{xc}\Big)\, \delta n\, \delta n'\ + \ \frac{1}{6} \int \Big(\frac{\delta^3 T_0}{\delta n \delta n' \delta n''} + L_{xc}\Big) \delta n\, \delta n'\, \delta n''\,, \quad (9)
\end{aligned}
$$

where it is implied that all functions are evaluated at $n = n_0$.

In this case $\delta T_0/\delta n + v_{xc} - \mu = 0$, and we get

$$
\begin{aligned}
\Omega[n, w] &= \Omega_0 + \int \delta w\, \delta n\ + \ \frac{1}{2} \int \Big(\frac{\delta^2 T_0}{\delta n \delta n'} + v + K_{xc}\Big)\, \delta n\, \delta n'\ + \\
&\quad \frac{1}{6} \int \Big(\frac{\delta^3 T_0}{\delta n \delta n' \delta n''} + L_{xc}\Big) \delta n\, \delta n'\, \delta n''\,,
\end{aligned} \tag{10}
$$

As noted above, the Eq.(10) is valid for arbitrary changes δw and δn. The physical value for Ω is, however, obtained when Ω is stationary with respect to density variations at a fixed potential δw. In this way density variations become coupled to potential variations. $\delta\Omega/\delta n = 0$ gives:

$$
\delta w + \int (v + K_{xc})\, \delta n' + \frac{1}{2} \int L_{xc}\, \delta n'\, \delta n'' + \int \frac{\delta^2 T_0}{\delta n\, \delta n'}\, \delta n' + \frac{1}{2} \int \frac{\delta^3 T_0}{\delta n\, \delta n'\, \delta n''}\, \delta n'\, \delta n'' = 0
$$

By comparing with Eq.(4) we see that

$$
\delta V = -\int \frac{\delta^2 T_0}{\delta n\, \delta n'} \delta n' - \frac{1}{2} \int \frac{\delta^3 T_0}{\delta n\, \delta n'\, \delta n''}\, \delta n'\, \delta n''\,, \tag{11}
$$

and, by inserting Eq.(3) into Eq.(11) above we find

$$
\frac{\delta^2 T_0}{\delta n \delta n'} = -\chi_0^{-1}\,, \tag{12}
$$

and

$$
\frac{\delta^3 T_0}{\delta n \delta n' \delta n''} = \chi_0^{-1}\, \chi_0^{-1}\, \chi_0^{-1}\, \phi_0\,, \tag{13}
$$

by comparing successive orders in δV. Inserting Eqs.(11), (12), and (13) into Eq.(5) gives

$$
\phi = \chi\, \chi\, \chi\, (\chi_0^{-1}\, \chi_0^{-1}\, \chi_0^{-1}\, \phi_0\ +\ L_{xc})\,. \tag{14}
$$

Furthermore, inserting Eqs.(5),(6),(12),(13), and (14) into Eq.(10) above we then finally obtain after some rearranging

$$
\Omega = \Omega_0 + \frac{1}{2} \int \delta w\, \chi\, \delta w\ + \frac{1}{6} \int \phi\, \delta w\, \delta w\, \delta w \tag{15}
$$

3

Assuming translational invariance and Fourier-transforming we have

$$\Omega \;=\; \Omega_0 + \Omega^{(2)} + \Omega^{(3)} \,, \tag{16}$$

with

$$\Omega^{(2)} \;=\; \frac{1}{2}\sum_{\mathbf{q}} \chi(\mathbf{q})|\delta w(\mathbf{q})|^2 \,, \tag{17}$$

and

$$
\begin{aligned}
\Omega^{(3)} \;=\; &\frac{1}{6}\sum_{\mathbf{q}\mathbf{q}'}\Big[\phi_0(\mathbf{q},\mathbf{q}') + L_{xc}(\mathbf{q},\mathbf{q}')\,\chi_0(\mathbf{q})\,\chi_0(\mathbf{q}')\,\chi_0(\mathbf{q}'-\mathbf{q})\Big] \times \\
&\tilde{\epsilon}^{-1}(\mathbf{q})\,\delta w(\mathbf{q})\,\tilde{\epsilon}^{-1}(\mathbf{q}')\,\delta w(\mathbf{q}')\,\tilde{\epsilon}^{-1}(\mathbf{q}'-\mathbf{q})\,\delta w(\mathbf{q}'-\mathbf{q}) \,,
\end{aligned} \tag{18}
$$

where $\sum_{\mathbf{q}}$ is short for $\int d^3q (2\pi)^{-3}$. Here $\tilde{\epsilon}^{-1}(\mathbf{q}) = \chi_0^{-1}(\mathbf{q})\chi(\mathbf{q})$ and, according to Eq.(6), $\chi(\mathbf{q})$ is given by

$$\chi(\mathbf{q}) = \frac{\chi_0(\mathbf{q})}{1 \,-\, [v(\mathbf{q}) + K_{xc}(\mathbf{q})]\,\chi_0(\mathbf{q})} \,. \tag{19}$$

Note that all of the response-functions above have an explicit density-dependence (like $K_{xc}(\mathbf{q};n)$), which we have temporarily suppressed here since it is not of any importance for the reasoning above. We immediately see that the function $\tilde{\epsilon}^{-1}$ ensures a well-behaved integrand in Eq.(18) above, even when δw is a point charge ($\delta w = -4\pi/q^2$).

Since we intend to compare infinite-order calculations based on the Local-Density Approximation (LDA), consistency requires us to use the LDA versions of the response functions:

$$
\begin{aligned}
v_{xc}^{LDA} \;&=\; \frac{\partial(n\epsilon_{xc})}{\partial n} = \mu_{xc}\,, \\
K_{xc}^{LDA}(\mathbf{q};n) = K_{xc}(0;n) \;&=\; \frac{\partial^2}{\partial n^2}(n\epsilon_{xc})\,, \\
L_{xc}^{LDA}(\mathbf{q},\mathbf{q}';n) = L_{xc}(0,0;n) \;&=\; \frac{\partial^3}{\partial n^3}(n\epsilon_{xc})\,,
\end{aligned} \tag{20}
$$

where ϵ_{xc} is the exchange-correlation energy per electron.

2.2 A simplified method for calculating the third-order energy.

The first term, $\Omega_0^{(3)}$, of the third-order energy, $\Omega^{(3)}$, has the form

$$\Omega_0^{(3)} = \frac{1}{6}\sum_{\mathbf{q}\mathbf{q}'} \phi_0(\mathbf{q},\mathbf{q}')\,\tilde{W}(\mathbf{q})\,\tilde{W}(\mathbf{q}')\tilde{W}(\mathbf{q}'-\mathbf{q}) \,, \tag{21}$$

where $\tilde{W}(\mathbf{q}) = \tilde{\epsilon}^{-1}(\mathbf{q})\,\delta w(\mathbf{q})$, and where the second-order independent-particle response function has the explicit form

$$\phi_0(\mathbf{q},\mathbf{q}') = 4\sum_{\mathbf{k}} \frac{1}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}+\mathbf{q}'}} \left[\frac{n_{\mathbf{k}+\mathbf{q}} - n_{\mathbf{k}}}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}} - \frac{n_{\mathbf{k}+\mathbf{q}'} - n_{\mathbf{k}}}{\epsilon_{\mathbf{k}+\mathbf{q}'} - \epsilon_{\mathbf{k}}}\right] \,. \tag{22}$$

Here $\epsilon_{\mathbf{k}} = k^2/2$ and $n_{\mathbf{k}}$ is a Fermi-factor forcing the state designated by 'k' to be occupied. The response function ϕ_0 can be calculated analytically [6] but unfortunately it has many singularities that cause severe numerical problems in the 6-dimensional integral yielding

$\Omega_0^{(3)}$ [Eq.(21)]. Moreover, the expression given in Eq.(21) is not valid in the case of non-local angular-momentum dependent pseudo-potentials of the norm-conserving kind [7]. We will now demonstrate a modified way of obtaining $\Omega_0^{(3)}$ which has the merit of being numerically stable as well as easy to generalize to non-local perturbations. After some rearrangement and shifting of integration variables we find

$$
\begin{aligned}
\Omega_0^{(3)} &= 2 \sum_{\mathbf{qq'k}} \Big[\frac{n_{\mathbf{k}}(1 - n_{\mathbf{q}})(1 - n_{\mathbf{q'}})}{(\epsilon_{\mathbf{q}} - \epsilon_{\mathbf{k}})(\epsilon_{\mathbf{q'}} - \epsilon_{\mathbf{k}})} - \frac{(1 - n_{\mathbf{k}})n_{\mathbf{q}}n_{\mathbf{q'}}}{(\epsilon_{\mathbf{q}} - \epsilon_{\mathbf{k}})(\epsilon_{\mathbf{q'}} - \epsilon_{\mathbf{k}})} \Big] \times \\
&\quad \tilde{W}(\mathbf{k} - \mathbf{q})\, \tilde{W}(\mathbf{q} - \mathbf{q'})\tilde{W}(\mathbf{q'} - \mathbf{k}) \,.
\end{aligned}
\tag{23}
$$

We now expand $\tilde{W}(\mathbf{k} - \mathbf{q})$ in spherical harmonics according to

$$
\tilde{W}(\mathbf{k} - \mathbf{q}) = 2\pi \sum_L \tilde{W}_l(k, q)\, Y_L(\hat{\mathbf{k}})\, Y_L^*(\hat{\mathbf{q}}) \,,
\tag{24}
$$

where

$$
\tilde{W}_l(k, q) = \int_{-1}^1 \tilde{W}(\mathbf{k} - \mathbf{q})\, P_l(t)\, dt \,,
\tag{25}
$$

and where t is the cosine of the angle between $\mathbf{k}$ and $\mathbf{q}$, $\mathbf{q} \cdot \mathbf{k} = k\, q\, t$. In the equations above, $P_l(t)$ is a normal Legendre polynomial of order l, and L is short for (l, m), m being the azimuthal quantum number. The quantity Y_L is a spherical harmonic. Inserting these expansions into Eq.(23), all angular integrations can be performed - leaving only three integrals over the lengths of the vectors $\mathbf{k}$, $\mathbf{q}$, and $\mathbf{q'}$. We thus obtain:

$$
\begin{aligned}
\Omega_0^{(3)} &= \frac{2}{(2\pi)^6} \sum_l (2l + 1) \int \frac{k^2 q^2 q'^2\, dk\, dq\, dq'}{(\epsilon_{\mathbf{q}} - \epsilon_{\mathbf{k}})(\epsilon_{\mathbf{q'}} - \epsilon_{\mathbf{k}})} \times \\
&\quad \Big[n_{\mathbf{k}}(1 - n_{\mathbf{q}})(1 - n_{\mathbf{q'}}) - (1 - n_{\mathbf{k}})n_{\mathbf{q}}n_{\mathbf{q'}} \Big] \tilde{W}_l(k, q)\, \tilde{W}_l(q, q')\tilde{W}_l(q', k) \,.
\end{aligned}
\tag{26}
$$

In the case of non-local perturbations, the analytical form for ϕ_0 can not be used. Still, due to spherical symmetry, the problem of calculating $\Omega_0^{(3)}$ can be reduced to a three-dimensional integral without singularities. Numerically, we have found the resulting sum over angular momenta l to converge extremely fast. It is, in fact, enough to include contributions up to $l = 3$.

2.3. The exchange-correlation energy.

In the derivation of the full expression for the relaxation energy $\Omega - \Omega_0$ it was assumed that the exchange-correlation part could be expanded according to

$$
E_{xc}[n] = E_{xc}[n_0] + \int v_{xc}\delta n + \frac{1}{2} \int K_{xc}\delta n\, \delta n' + \frac{1}{6} \int L_{xc}\delta n\, \delta n'\, \delta n'' \,.
\tag{27}
$$

This is certainly the case for sufficiently small potentials, but not for the screened but still very strong potentials associated with point-charge perturbations. We have found, numerically, that the perturbation expansion for the kinetic energy T_0 (represented by the response functions χ_0 and ϕ_0) is much more robust as compared to the expansion of E_{xc}. Especially within the LDA, we have seen that terms involving higher-order derivatives with respect to density can produce entirely wrong results. This knowledge immediately suggests an alternative procedure. Since the full result for Ω, Eq.(15), involves the perturbation expansion for E_{xc}, we simply subtract that expansion and replace it with

the full result. Denoting by n_1 the first-order density change given by $n_1 = \chi \delta w$, we obtain, for instance,

$$\Delta_{xc} = E_{xc}[n_0 + n_1] - E_{xc}[n_0] - \mu_{xc} \int n_1 - \frac{1}{2} \int K_{xc} n_1 \, n_1 - \frac{1}{6} \int L_{xc} n_1 \, n_1 \, n_1 \, . \qquad (28)$$

By adding this correction to the full result we see that the problematic term involving the third density derivative (L_{xc}) disappears. Notice, however, that the resulting expression is still entirely correct to third order. The positive effect of adding the correction Δ_{xc} can be studied in Fig. 1. The errors are reduced from $\sim 10\%$ to $\sim 7\%$. We can go one step further and include in the correction also the second-order density given by [see Eqs.(5),(14)]

$$n_2 = \frac{1}{2} \chi \phi_0 \chi_0^{-1} \chi_0^{-1} \chi_0^{-1} \chi \chi \delta w \, \delta w \, \delta w \, , \qquad (29)$$

where we have deliberately dropped the term proportional to the response function L_{xc}. The correction then becomes

$$\begin{aligned}
\Delta'_{xc} &= E_{xc}[n_0 + n_1 + n_2] - E_{xc}[n_0] - \mu_{xc} \int (n_1 + n_2) - \\
&\quad \frac{1}{2} \int K_{xc} n_1 \, n_1 - \int K_{xc} n_1 \, n_2 - \frac{1}{6} \int L_{xc} n_1 \, n_1 \, n_1 \, .
\end{aligned} \qquad (30)$$

This correction is more difficult to apply due to the appearance of the second-order density n_2, but our preliminary results indicate that the total error is now reduced to some $4 - 5\%$ over the entire metallic range, $r_s = 2 - 5.5$. Here, r_s is the radius of a sphere containing one electron.

3. Results.

Our first test-case is a unit point-charge inserted into the electron gas of different densities given in terms of the usual parameter r_s. Physically this would approximately correspond to, *e.g.*, hydrogen impurities immersed in simple metals. It should be stressed that this constitutes a severe test on the perturbation approach. A proton does not furnish the exchange repulsion normally associated with singly charged positive ions. Moreover, the electrons of the homogeneous gas are easier to displace as compared to the case of real solids, in which electrons have a relatively large probability of sticking to a particular atom.

Nevertheless, the results are moderately encouraging, as seen in Fig. 1 displaying the relaxation energy as a function of r_s. Taking $r_s = 3$ as a typical density in the metallic range we see that, within linear response, the result is $\sim 33\%$ too small in magnitude. Adding the third-order contribution reduces the error to 9%. Adding also a correction due to treating the exchange-correlation energy in a non-perturbative way, as described in Sec. 2.3., the error drops to 7%. This correction should really have included also the second-order density and our preliminary results indicate that the error then drops to 5%. Since the total relaxation energy in this case is $13.3 eV$, the error is $0.7 eV$ which is somewhat on the large side. We would thus hesitate to treat the case of say, an alpha-particle (He^{2+}) in the gas within third-order perturbation theory.

Maybe a somewhat more useful test case is that of a gas in which we have inserted a singly-charged ion, here represented by a pseudo-potential. The latter is chosen to correspond closely to a sodium ion and it is local, but still very close to norm-conserving.

It is given in terms of a Gaussian and an r^2 - multiplied Gaussian as described in Ref. [8]. It reproduces the $3s$ and $3p$ eigenvalues of the sodium atom. The relaxation energy as a function of r_s is shown in Fig. 2. Already linear response gives an accurate result and the addition of the third-order contribution makes the curve almost indistinguishable from the exact one. In particular we see from the enlarged insert that the third-order contribution accurately accounts for the difference between the second-order result (linear response) and the exact curve. In this example the results are very accurate and we have not bothered about adding small corrections intended to improve the description of exchange and correlation as described in our first example. We conclude this paragraph with the remark that our sodium example physically corresponds to a sodium ion added interstitially into a simple metal. Again this can be considered a strong perturbation, at least compared to the problem of calculating phonon frequencies. In the latter problem one displaces pseudo-potentials rather than inserting them. In such cases the perturbative approach should thus be more than adequate.

As our third and final example we have immersed a doubly charged positive ion in an electron gas. What we have in mind is a Mg^{2+} - ion in different simple metals, and our constructed pseudo-potential for this case is again local and almost norm-conserving. For this case we have, so far, only performed a series of calculations up to $r_s = 2$. The picture that emerges is, however, very similar to that of the singly charged case (sodium above). The linear response result is already quite accurate and the third-order contribution, which is largest in the high-density regime, gives a very accurate description of the difference between the infinite-order and the second-order results. The total error is less than 2%.

4. Conclusions and outlook.

In the present work we have studied the accuracy of third-order perturbation theory as applied to the insertion of protons and charged ions into simple metals modeled by an electron gas. We have found that a proton represents such a strong perturbation that it can just barely be described within third-order response theory. We speculate that a proton in an electron gas constitute a stronger perturbation than a proton interstitially placed in a crystal structure. Consequently, we believe the latter problem to be well within the realm of third-order perturbation theory. The case of alpha-particles, *i.e.*, He^{2+} - ions in solids is, however, believed to be outside the validity of third-order perturbation theory.

We have also found that singly or doubly charged positive ions represented by pseudo-potentials are well described by the present theory, and we argue that negative ions can be even better described. This is because the repulsive character of the Coulombic tail keeps the responding electrons away from the strong core of the pseudo-potential. We also have some preliminary results indicating that stronger pseudo-potentials resulting from the requirement of a very high transferability [8], will cause problems in a perturbative treatment. In such cases one should very carefully remove the unphysical energies associated with the repulsive cores of the pseudo-potentials. How this can be done in a consistent way will be described in a forthcoming publication. Finally we again stress that the investigation reported in the present article is part of a wider project to assess the utility of perturbative methods to a number of physical problems. Later publications will, *e.g.*, deal with periodic perturbations of the electron gas or the representation of localized d - electrons in terms of pseudo-potentials for later application of the perturbative method.

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Figure captions:

Figure 1: Non-linear screening of a bare proton inserted in an electron gas. Full relaxation energy, $\Delta\Omega$, versus the relaxation energy to second-, $\Omega^{(2)}$, third-order, $\Omega^{(2)} + \Omega^{(3)}$, and with correction $\Omega^{(2)} + \Omega^{(3)} + \Delta_{xc}$ as given by Eq.(28).

Figure 2: Same properties given as in Fig. 1, but in this case for a pseudo-potential describing a singly charged ion. Note the enlarged quantities in the upper half of the figure, demonstrating the accuracy of the third-order contribution.
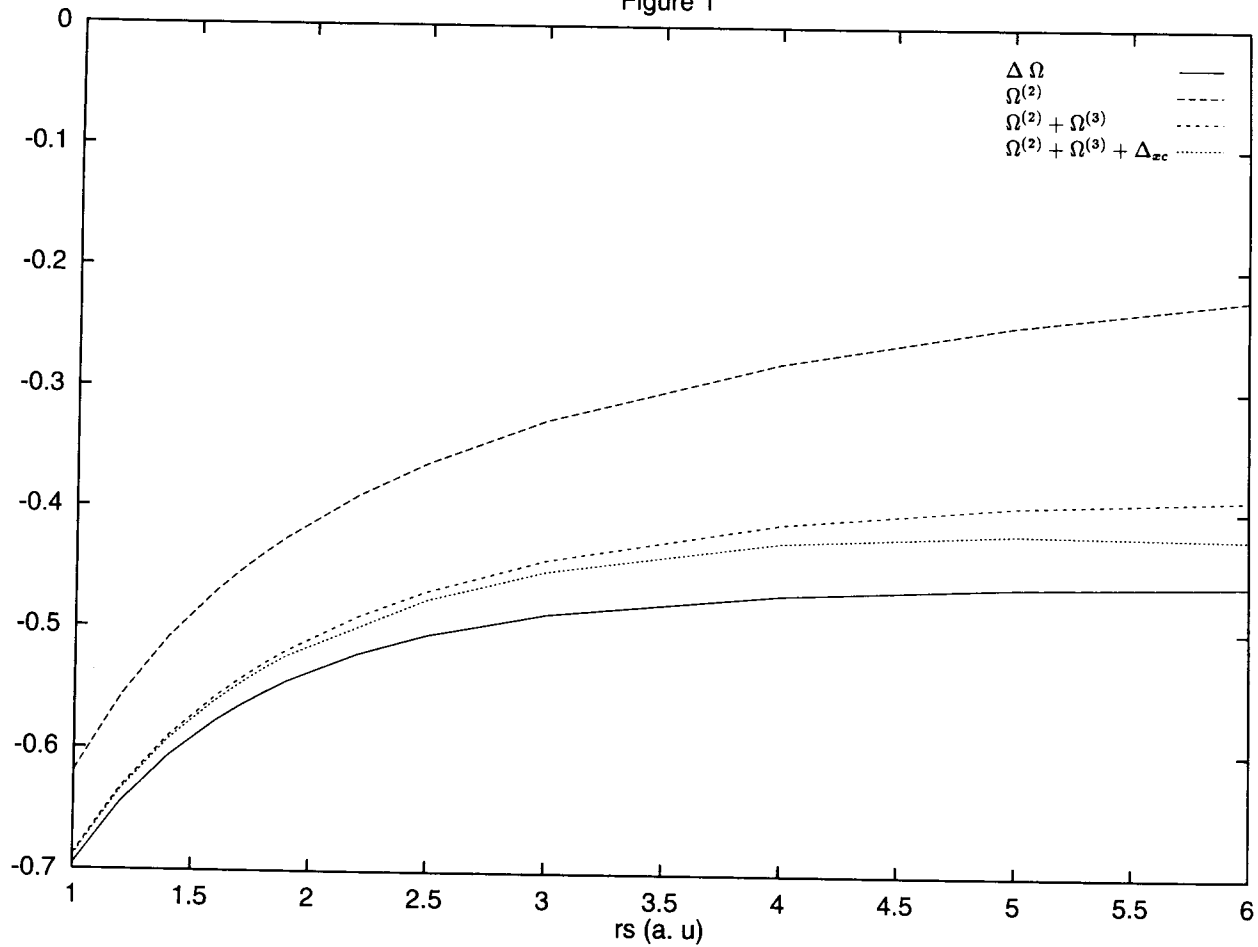
Figure 1

Figure 2