The von Weizsäcker Coefficient in Density Functional Theory [†]

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For any given potential, linear response theory tells us the size that the von Weizsäcker coefficient must assume in order to obtain the correct energy in the weak coupling limit. With this necessarily imposed choice, the quality of results is investigated as the coupling is strengthened. From the study of a number of model problems (the harmonic oscillator, the Yukawa well and the Mathieu potential) it is concluded that good results can be maintained to high couplings.

1. Introduction

The appeal of density functional methods in the quantum-mechanical manybody problem is that they offer relatively simple equations to be solved. The example, par excellence, of this assertion is the Thomas-Fermi theory which, though very simple, is unfortunately too crude for many purposes. Consequently there has been, since the early days of quantum mechanics a sustained interest in possible improvement of this technique.

One of the earlier suggestions is due to von Weizsäcker [1] who introduced a contribution to the kinetic energy density depending upon the gradient of the particle density. This modification has been used often, examples of recent applications being to the energetics of pure metallic lattices by Meyer, Umar and Young [2] and of rare gas atoms implanted in the noble metals by Citrin and Hamann [3].

Long after von Weizsäcker's original paper, it was proposed by Kompaneets and Pavlovskii [4] and Kirzhnits [5] that while the Weizsäcker functional form should be retained, its size should be reduced by a factor of nine. In this modified form, the method has also found many applications. For example, in this way, Smith [6] and Appelbaum and Baraff [7] have studied metallic surfaces, Hodges and Stott [8] alloys and Santos and Villagrá [9] the interlayer problem in graphite.

Despite a number of subsequent alternative derivations of the modified theory (see, for example, Hohenberg and Kohn [10], Stoddart, Beattie and March [11]) it has not been clear, a priori, what coefficient to choose in any given problem, though the overall trend seems to have been to use the reduced coefficient without justification. The situation was clarified somewhat by Jones and Young [12] who showed that, for weak coupling, the newer version of the theory was correct for external potentials containing only long wavelength components. On the other hand, for potentials containing only short wavelength components, the original von Weizsäcker coefficient was demonstrated to be correct.

In practice, inevitably, we face the problem of strong potentials containing components distributed over all wavelengths. Even in the weak coupling limit it is clear, in general, from Jones and Young's work, that the coefficient which gives the energy exactly will not be precisely correct for, say, the particle density, and this has led Hodges [13] to generalize the von Weizsäcker functional form itself.

Despite the above shortcoming, it is true, nonetheless, that for any given external potential, a suitably modified von Weizsäcker coefficient can be defined, a priori, to give the correct energy provided the coupling is sufficiently weak. In the present paper we ask the question whether, once this coefficient is chosen, the von Weizsäcker formalism will continue to give good energies as the coupling strength is increased.

To help answer this question we have studied, by the above technique, a number of model systems (the harmonic oscillator, the Yukawa well and the Mathieu potential) for which exact results can be found. The latter, of course, are for non-interacting particles as must, therefore, be the approximate results. But this is no drawback; the point at issue is the definition and efficacy of the kinetic energy

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functional, the potential energy functional constituting a quite separate problem.

In the following section, we introduce the formalism and define the coupling constant in terms of the potential. Then in Sections 3, 4 and 5 we present the results for the three model systems referred to above. Finally, in Sect. 6, we state our conclusion.

2. The von Weizsäcker Coefficient

Suppose we have N independent fermions moving in a volume Ω. The common fixed external potential is $v(\boldsymbol{r})$. The exact ground state energy for this problem is obtained by adding the single-particle eigenvalues for the lowest doubly-occupied levels; the exact density is found by summing the corresponding single-particle densities.

On the other hand, the von Weizsäcker method tells us to minimize the energy functional ($\hbar = m = 1$, throughout)

$$E_\lambda = \int \left\{ \frac{3}{10} (3\,\pi^2)^{2/3}\, n^{5/3} + \frac{\lambda}{8} \frac{(\nabla n)^2}{n} + n\,v \right\} \mathrm{d}r \tag{1}$$

where, here n plays the role of the density. In his original formulation, von Weizsäcker[1] obtained $\lambda = 1$; subsequently Kirzhnits[5] and Kompaneets and Pavlovskii[4] suggested $\lambda = 1/9$.

As Jones and Young[12] pointed out, when v is sufficiently weak, the energy can be calculated exactly to second order and compared with the prediction found by linearizing Equation (1). Writing

$$v(\boldsymbol{r}) = \frac{1}{\Omega} \sum_{\boldsymbol{q}} \tilde{v}(\boldsymbol{q}) \exp\{-i\,\boldsymbol{q}\cdot\boldsymbol{r}\}; \tag{2}$$

we obtain the expression

$$E = \frac{3}{10} N\,k_{\mathrm{F}}^2 + n_0\,\tilde{v}(0) - \frac{k_{\mathrm{F}}}{2\,\pi^2\,\Omega} \sum_{\boldsymbol{q}\neq 0} f(\eta)\,|\tilde{v}(\boldsymbol{q})|^2 + \ldots \tag{3}$$

where $n_0 = N/\Omega$ and $k_{\mathrm{F}}^3 = 3\,\pi^2\,n_0$. The result based on Eq. (1) corresponds to

$$f_\lambda(\eta) = \frac{1}{1 + 3\,\lambda\,\eta^2}\,; \quad \eta = \frac{q}{2\,k_{\mathrm{F}}} \tag{4}$$

while the exact result is

$$f(\eta) = \frac{1}{2}\left(1 + \frac{1-\eta^2}{2\,\eta} \ln \left|\frac{1+\eta}{1-\eta}\right|\right). \tag{5}$$

If the approximate method is to give the exact energy in the weak coupling limit then, as Eq. (3) indicates, we require

$$\int \{f_\lambda(\eta) - f(\eta)\}\,|\tilde{v}(\boldsymbol{q})|^2\,\mathrm{d}\boldsymbol{q} = 0\,. \tag{6}$$

This is our defining equation for λ; the solution is independent of any coupling constant factor contained in v.

If Eq. (2) contains only Fourier components corresponding to $\boldsymbol{q}$'s of the same modulus q_0 then Eq. (6) solves to give

$$\lambda = \frac{1 - f(\eta_0)}{3\,\eta_0^2\,f(\eta_0)}\,. \tag{7}$$

This function $\lambda(\eta_0)$ is plotted in Fig. 1; its one-dimensional equivalent will be considered in relation to the Mathieu problem in Section 5.

In general, however, Eq. (6) defines λ implicitly for any given potential. The method we investigate then, is to solve Eq. (6) for λ and then use this λ in Eq. (1) to investigate E_λ as the coupling constant in v is made large. The results for a number of different potentials are presented in the following sections.

3. The Harmonic Oscillator

As a first example, we consider the potential

$$v(r) = \tfrac{1}{2}\,k\,r^2\,e^{-ar}, \quad \tilde{v}(q) = \frac{48\,\pi\,k\,a}{q^6} \frac{\{(a/q)^2 - 1\}}{\{(a/q)^2 + 1\}^4} \tag{8}$$

where k is a coupling constant. Substitution of Eq. (8) into Eq. (6) and solving numerically for λ gives results which are shown in Figure 2.

We find that as $a/2\,k_{\mathrm{F}}$ increases from 0, λ increases from 0.1111. The reason for this behavior

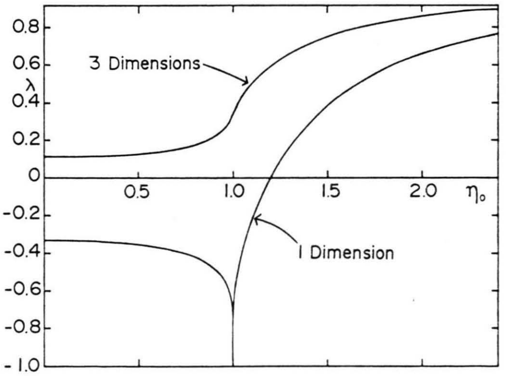

Fig. 1. The von Weizsäcker coefficient λ which gives the correct weak coupling limit when the potential contains only Fourier components of modulus $2\,k_{\mathrm{F}}\,\eta_0$. In one dimension, $\lambda(1) = -1$.

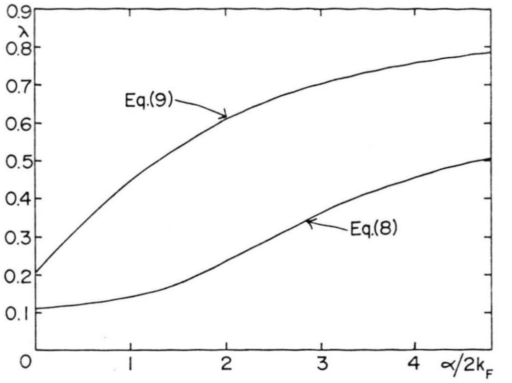

Fig. 2. The von Weizsäcker coefficient λ which gives the correct energy in the weak coupling limit when the potentials are given by Eqs. (8) and (9).

is that when a is small, the small q components in $v(q)$ are dominant and thus Eq. (6) solves to give a λ characteristic of the long wavelength limit shown in Figure 1. When a is large, $\tilde{v}(q)$ is independent of q, in leading order. Thus, the volume element in Eq. (6) ensures that λ will become representative of short wavelengths and approach the value of unity indicated in Figure 1.

In the limit $a \to 0$ we obtain the harmonic oscillator well for which, of course, exact results are known and for which Eq. (1) has been minimized by Berg and Wilets[14]. They found empirically (see, also, March[15]) that $\lambda \sim 1/8$ was required for E_λ to give the exact energy for large numbers of particles. This is in essential agreement with the present prescription which tells us to use $\lambda = 0.1111$ for this problem. The need for the highly reduced coefficient is dictated by the overwhelming importance of small q Fourier components in the potential.

4. The Yukawa Well

In this case we take

$$V(r) = \frac{z}{r} \exp\{-a\,r\}; \quad \tilde{v}(q) = \frac{4\pi z}{q^2 + a^2}. \tag{9}$$

Such expressions have been used often to approximate the self-consistent potential associated with a point charge of z electronic charges screened by an electron gas. Formally, z does not have to be an integer and here it plays the role of the coupling parameter considered, in the first instance, in the derivation of Eq. (6), to be weak.

Substitution of Eq. (9) into Eq. (6) and solving numerically for λ gives results which are shown in Figure 2. There is one interesting difference from those based on Equation (8). When $a/2\,k_F \to \infty$, small wavelengths dominate and $\lambda \to 1$, as before. However, when $a/2\,k_F \to 0$, we find $\lambda \to 0.205$ instead of the value of 1/9 suggested by Figure 1. This is because $q^2\,v(q)$ becomes independent of q as $a \to 0$ so that long wavelengths never predominate (as they did in the corresponding harmonic oscillator limit). As before, we now ask how accurate the results are when used in Equation (1).

In the limit $a \to 0$ we have the Coulomb field problem for which exact results can be calculated. Yonei and Tomishima[16] studied the minimization of Eq. (1) for the neutral "atom" cases $z = N$ and found that to reproduce the exact energies they required λ to vary from 0.25 for $N = 10$ to 0.20 for $N = 90$. Our procedure, which requires $\lambda = 0.205$ in the $N = \infty$ limit would thus appear to give good results for this problem even though the original weak coupling reference system has been radically transformed.

There are also indications that Fig. 2 leads to realistic conclusions when a is non-zero. March and Murray[17] calculated essentially exact results for a potential close to Eq. (9) with $z = -1$ and $a/2\,k_F = 0.665$ (the linearized Thomas-Fermi value appropriate to copper) and compared them with a corresponding von Weizsäcker ($\lambda = 1$) study. They concluded that λ needed to be much reduced from unity.

Unfortunately, it is not possible to obtain, from their work, a quantitative estimate of the λ required to get the energy right. However, they found that the displaced charge from a sphere of radius 2.66 atomic units (the Wigner-Seitz radius for copper) was 0.47 electronic charges whereas the corresponding von Weizsäcker ($\lambda = 1$) and Thomas-Fermi ($\lambda = 0$) results were 0.56 and 0.44 respectively. Linear interpolation thus suggests a correct λ of about 0.25.

According to the present prescription, we would choose $\lambda = 0.38$. This is certainly in qualitative agreement with March and Murray's conclusion that λ should be substantially reduced from unity. Indeed, considering the various uncertainties involved in arriving at the 0.25 result above, the a priori figure of 0.38 might be deemed to be at least semi-quantitatively correct.

5. The Mathieu Potential

Here, we have considered the one-dimensional case

$$v(x) = A\cos(q_0 x)\,; \quad \tilde{v}(q) = \tfrac{1}{2} A\,L(\delta_{q,q_0} + \delta_{q,-q_0}) \tag{10}$$

where L is the length of the box. For this problem, $k_F = \pi N/2L$ (doubly-occupied levels) and the reciprocal lattice vectors are given by $n\,q_0$ where $n = 0, \pm 1, \pm 2, \dots$.

The exact solution for the total energy is obtained by first solving (numerically) the secular equation

$$\det\left|\{\tfrac{1}{2}(k - n\,q_0)^2 - E(k)\}\,\delta_{nn'} + L^{-1}\,\tilde{v}(n\,q_0 - n'\,q_0)\right| = 0 \tag{11}$$

and then computing

$$\frac{E}{N} = \frac{1}{2\,k_F}\int_0^{k_F} E(k)\,dk\,. \tag{12}$$

The one-dimensional equivalent of Eq. (1) is

$$E_\lambda = \int\left\{\frac{\pi^2}{24}\,n^3 + \frac{\lambda}{8}\,\frac{(dn/dx)^2}{n} + n\,v\right\}dx \tag{13}$$

and of Eq. (3) is

$$E = \frac{1}{6}\,N\,k_F^2 + n_0\,\tilde{v}(0) - \frac{1}{\pi\,k_F\,L}\sum_{q\neq 0} f(\eta)\,|\tilde{v}(q)|^2 \tag{14}$$

where now, instead of Eq. (4) and Eq. (5) we have

$$f_\lambda(\eta) = 1/(1 + \lambda\,\eta^2)\,; \quad \eta = q/2\,k_F \tag{15}$$

and

$$f(\eta) = \frac{1}{2\,\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|.$$

For the special potential Eq. (10), the one-dimensional equivalent of Eq. (6) solves explicitly for λ (recall the penultimate paragraph of Sect. 2) and we obtain

$$\lambda = \frac{2}{\eta_0 \ln\left|\dfrac{1+\eta_0}{1-\eta_0}\right|} - \frac{1}{\eta_0^2} \tag{17}$$

where $\eta_0 = q_0/2\,k_F$. This is the analogue of Equation (7). The function defined by Eq. (17) is plotted in Fig. 1 and can be contrasted in a number of ways with the three-dimensional result.

First, for some smaller values of η_0, λ is negative. As far as we know, this is the first example in the literature where the introduction of a von Weizsäcker term is necessary to reduce the energy. A usual physical argument for the introduction of the term is that it prevents excessive variations in the density; for example, without it the resulting Thomas-Fermi method produces divergences in n should divergences occur in v. Such an argument, of course, relies on λ being positive. Figure 1 shows that any one-dimensional potential dominated by Fourier components of sufficiently long wavelengths requires a negative λ.

Other points worthy of note are the cusp at $\eta_0 = 1$, $\lambda = -1$ and the fact that while $\lambda \to 1$ when $\eta \to \infty$, as in three dimensions, the opposite limit of $\eta_0 = 0$ now corresponds to $\lambda = -\frac{1}{3}$, in contrast with the three-dimensional result $\lambda = \frac{1}{9}$.

Turning now to the minimization of Eq. (13), we chose (arbitrarily) $A = 0.1\,q_0^2$ and calculated, as functions of k_F, results for the usual von Weizsäcker case, $\lambda = 1$, and the Thomas-Fermi case $\lambda = 0$. The details of the procedure involved are given in the Appendix and the results are shown in Figure 3.

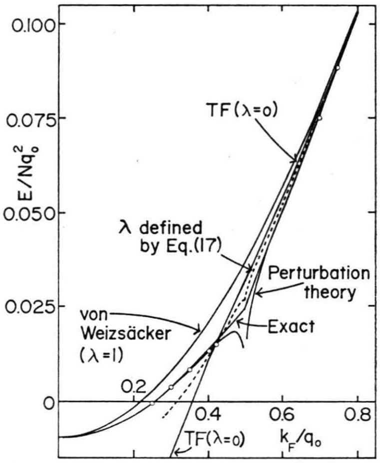

Fig. 3. Energy versus Fermi wave index for the Mathieu problem given by Eq. (10) with $A = 0.1\,q_0^2$. The broken line corresponds to linear interpolation or extrapolation of the $\lambda = 0,1$ results on choosing λ in accordance with Equation (17). The circles correspond to the proper procedure of optimizing Eq. (13) with λ chosen via Equation (17).

It is of interest to note, in passing, that despite being non-linear, the von Weizsäcker method (always) and the Thomas-Fermi method (nearly always) are inferior, in this application, to second-order perturbation theory (except in the immediate vicinity of the Brillouin zone edge, $k_F = \frac{1}{2}\,q_0$, where the latter diverges).

Knowing the energies for $\lambda = 0$, it is possible to infer, by linear interpolation or extrapolation, approximate results for the choice of λ indicated by Eq. (17) and Figure 1. Such data are shown in Figure 3. Alternatively, we might attempt direct calculations [by finding λ from Eq. (17) and then optimizing Eq. (13)]. In the regions away from the zone edge, the direct method improves on the results obtained by linear interpolation, as Fig. 3 shows, but near this edge we are unable to find satisfactory solutions. It is not clear whether the deficiency is one of technique or principle and we leave the question open of whether an approach like the present one can describe band gap characteristics. Certainly there is promise and such an aspiration has been beyond density functional methods hitherto. Leaving aside this unresolved matter, it will be seen that the specification of λ via Eq. (17) does, in general, lead to improvements over the Thomas-Fermi and ($\lambda = 1$) von Weizsäcker results.

6. Conclusion

We have given a prescription [Eq. (6)] for choosing, a priori, the von Weizsäcker coefficient appropriate to any given problem of non-interacting particles moving in a common potential. This has been tested on a few cases where some information is obtainable about the exact solutions. These tests suggest that the present method is a useful way of specifying the coefficient. Indeed it is difficult to imagine as simple a prescription which will do better.

All this is assuming, of course, that N is very large. When N is not large there are good reasons for reducing the size of the Fermi coefficient [the first term of Eq. (1)], as has been recognized by Gombás[18, 19] and March and Young[20]. Recently a very detailed study of possible modifications of this type has been made Szasz, Berrios-Pagan and McGinn[21] and since we have here studied modifications in the von Weizsäcker coefficient, our paper complements theirs.

The problem of interacting particles has not been considered in the present work. For, as mentioned earlier, the introduction of interactions is a sophistication superposed on the non-interacting case in which the problem of handling the kinetic energy density functional has already arisen. However, it is easy to see how such a case could be considered. A suitable generalization of Eq. (1) may be written down and linearized so as to obtain a revised form of f_λ instead of Equation (4). On the other hand, accurate forms of f are known from electron-gas linear response theory (see, for example, Hedin and Lundqvist[22]) and such an expression can replace Equation (5). From then on, the method would proceed much as before.

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Appendix 1

Here, we show how Eq. (13) was minimized for the potential Equation (10). First, the change of variable $q_0 x = y$ and of function $n(x) = 2 k_F \psi^2(y)$ gives

$$\frac{E_\lambda}{N} = k_F^2 \int_0^\pi \left\{ \frac{\pi^2}{6} \psi^6 + 2 \lambda \eta_0^2 (\psi')^2 + \left(\frac{A}{k_F^2} \cos y \right) \psi^2 \right\} dy . \tag{A1}$$

This has to minimized subject to the normalization requirement

$$\int_0^\pi \psi^2 \, dy = 1 . \tag{A2}$$

The appropriate Euler equation is

$$-\tfrac{1}{2} \lambda \psi'' + \frac{\pi^2}{8 \eta_0^2} \psi^5 + \left(\frac{A}{q_0^2} \cos y \right) \psi = \varepsilon \psi \tag{A3}$$

ε defining the chemical potential. Equation (A3) is a kind of effective Schrödinger equation for the total density amplitude (Gombás[23]). The boundary conditions are $\psi'(0) = \psi'(\pi) = 0$.

For any ψ satisfying Eq. (A3), Eq. (A1) reduces to

$$\frac{E_\lambda}{N} = k_F^2 \left\{ \varepsilon - \frac{\pi^2}{3} \int_0^\pi \psi^6 \, dy \right\} . \tag{A4}$$

Thus, once Eq. (A3) is solved, it is easier to use Eq. (A4) than Eq. (A1) to find E_λ.

For specified λ, A and k_F, our numerical procedure was as follows. First, a value for ε was guessed. With this ε, Eq. (A3) was solved (by trial and error) until a solution satisfying the boundary conditions was obtained. Using this solution, Eq. (A2) was tested; in general the normalization was found to be incorrectly given. So, revised values of ε were taken until Eq. (A2) was satisfied. With the corresponding ψ, Eq. (A2) was evaluated.

The Thomas-Fermi case ($\lambda = 0$) requires separate consideration. Then provided $\varepsilon \geqq A$, Eq. (A3) solves explicitly for ψ over the whole range. When $\varepsilon < A$, the same form of solution holds in the classically accessible region; elsewhere $\psi = 0$.

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