QUASI-LOCAL-DENSITY APPROXIMATION FOR A VAN DER WAALS ENERGY FUNCTIONAL
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ABSTRACT

We discuss a possible form for a theory akin to local density functional theory, but able to produce van der Waals energies in a natural fashion. The usual Local Density Approximation (LDA) for the exchange and correlation energy $E_{xc}$ of an inhomogeneous electronic system can be derived by making a quasilocal approximation for the interacting density-density response function $\chi(\vec{r}, \vec{r}', \omega)$, then using the fluctuation-dissipation theorem and a Feynman coupling-constant integration to generate $E_{xc}$. The first new idea proposed here is to use the same approach except that one makes a quasilocal approximation for the bare response $\chi^0$, rather than for $\chi$. The interacting response is then obtained by solving a nonlocal screening integral equation in real space. If the nonlocal screening is done at the time-dependent Hartree level, then the resulting energy is an approximation to the full inhomogeneous RPA energy: we show here that the inhomogeneous RPA correlation energy contains a van der Waals term for the case of widely-separated neutral subsystems. The second new idea is to use a particularly simple way of introducing LDA-like local field corrections into the screening equations, giving a theory which should remain reasonable for all separations of a pair of subsystems, encompassing both the van der Waals limit much as in RPA and the bonding limit much as in LDA theory. The resulting functional is an explicit recipe which takes a trial electron density distribution $n(\vec{r})$ as its input and yields $E_{xc}$ as its output. The reason that it includes the van der Waals energy is that, like the RPA formalism but unlike LDA, it involves spatially nonlocal screening for inhomogeneous systems. It differs from earlier theories which effectively use hydrodynamics to generate $\chi^0$, in that rapid spatial variations in electron density, such as those at subsystem boundaries, can be handled more effectively; LDA-like local correlations are also included. Thus the theory has credibility even at small separations outside.
the traditional asymptotic van der Waals limit. We can therefore hope for a consistent description of the forces between subsystems such as molecules or metal surfaces, equally reasonable at all separations from the chemical bonding regime through to the nonretarded van der Waals limit.

1. INTRODUCTION

Jay Mahanty is well known for his pioneering work on van der Waals (“vdW” or “dispersion”) forces [1-7], and the present paper is presented as a tribute in the form of a possible extension of his methods. Perhaps the most familiar example of a dispersion force is the attractive interaction between a widely separated pair of neutral atoms, which is proportional to \(1/R^6\) in the nonretarded regime and to \(1/R^7\) in the retarded regime, where \(R\) is the interatomic separation. More generally, dispersion forces become important in the interaction between electrically neutral subsystems at separations larger than a few Angstroms so that electron transport between the subsystems is negligible. The present paper attempts to generalise existing theories of the van der Waals interaction to cases where the separation is not necessarily large compared with atomic dimensions, so that the interaction between the subsystems cannot be treated perturbatively. In this regime one has to consider Angstrom-scale details of the electron distribution at the edges of the subsystems. For a description of electronic behaviour on such short spatial scales one cannot rely upon the hydrodynamic arguments which have recently been popular in the van der Waals context, so a more microscopic theory is required. An additional motivation for the present paper is the suggestion [4,8-11] that van der Waals phenomena can be important even in large connected regions of high electronic density (e.g., bulk metals) for which van der Waals phenomena have not traditionally been considered.

The van der Waals energy is relevant in the interaction between neutral systems in the domain where the separation is greater than a few Angstroms, but less than the wavelength of light at the dominant fluctuation frequencies so that electromagnetic retardation effects [1,3,5] can be ignored. The vdW interaction can be derived, for example, by second-order perturbation theory in the coulomb interaction between the two species [1], or by an RPA-like fluctuation-dissipation theorem argument involving the electric polarisability, which will be discussed further below. On the other hand, for quantum systems in close contact, the simplest reasonably successful general theory describing the Pauli repulsion and bonding forces is the Local Density Functional theory of Kohn and Sham, together with improvements by a number of workers [12,13]. The local density functional expression for the exchange-correlation energy misses the van der Waals interaction, however, and RPA calculations are not reliable for bonding situations nor for extended systems at metallic densities. There is therefore a need for a theory which works in all regimes. Ashcroft and co-workers [8-11] have recently suggested ways of including van der Waals effects
in a density functional framework. In the present paper we suggest a rather
different quasi-local density formalism which should reproduce the vdW force
between widely separated species but which remains well-defined as the species
are brought together. It makes use of a prior calculation of the dynamic elec-
tronic susceptibility of the uniform electron gas.

The new method will now be developed as follows. Firstly, in section 2 the
RPA groundstate energy formalism is reviewed for the case of an inhomoge-
neous electronic system: this amounts to a time-dependent Hartree or mean-
field evaluation of the inhomogeneous dynamic susceptibility \( \chi \) followed by use
of the fluctuation-dissipation theorem in order to generate approximate pair
correlations. A coupling-constant integration is also involved. Then in section
3 it is shown that the vdW interaction between separated neutral systems is
reproduced by the RPA formulation described in Section 2. In Section 4 it is
pointed out that the essential element in producing the vdW energy term is not
the nonlocality of the bare susceptibility \( \chi^0 \) (which merely reflects independent
electron transport, a phenomenon not involved in the vdW interaction). Rather,
the essence of the vdW interaction stems from nonlocality of the selfconsistent
Coulomb screening (Hartree) integral equation, which allows distant density
fluctuations to interact. It is therefore proposed to make a suitable local or
quasi-local approximation for \( \chi^0 \), followed by solution of the nonlocal Coulomb
screening integral equation to produce an interacting susceptibility \( \chi \). Finally
one uses the fluctuation-dissipation theorem and a coupling-constant integra-
tion. This approach leads to an explicit though fairly cumbersome procedure
for obtaining a total energy including the vdW contribution, starting from a
given static density \( n(r) \). This expression is merely an approximation to the
full RPA energy and does not include the local field corrections inherent in, for
example, the Kohn-Sham exchange-correlation functional. To remedy this omis-
sion we propose in section 5 a way to include LDA-like local field corrections
alongside the RPA effects already introduced. A summary is given in Section 6.

2. SUMMARY OF THE RPA GROUNDSTATE ENERGY FORMALISM

Since it is being asserted that the vdW interaction is inherent in the inhomo-
geneous RPA correlation energy formalism, we begin by stating exactly what
is meant here by this formalism. To calculate the RPA linear response of an
interacting system one first solves the selfconsistent Hartree groundstate equa-
tions [14] to yield a selfconsistent potential \( V_0(r,s) \), plus a set of one-particle
orbitals \( \varphi_i(r,s) \) and eigenvalues \( \epsilon_i \). Then from first-order perturbation theory
one forms [20] the bare susceptibility

\[
\chi^0(r, r', \omega) = \sum_{i,j,s} (f_i - f_j) \left( \varphi_i^*(r, s) \varphi_j^*(r', s) \varphi_j(r, s) \varphi_i(r', s) \right) \frac{\epsilon_i - \epsilon_j - \hbar \omega}{\epsilon_i - \epsilon_j - \hbar \omega}.
\]
where $s$ labels the spin projection eigenvalue of a state. Physically, $\chi^0$ represents the linear response, to an external potential $\delta V(\vec{r}) \exp(-i\omega t)$, of a system of independent electrons moving in the static potential $V^{\text{0th}}(r)$: i.e.

$$\delta n^{\text{indep}}(\vec{r}, t) = \exp(-i\omega t) \int \chi^0(\vec{r}, \vec{r}', \omega) \delta V(\vec{r}') d^3r' \tag{2}$$

The general form of (2) is dictated by the fact that it is the most general possible linear time-invariant connection between the density perturbation $\delta n$ and the potential $\delta V$ which causes it. The fact that $\chi^0$ is spatially nonlocal (i.e. connects different “density” and “potential” points $r$ and $r'$) is solely due to the motion (“transport”) of individual electrons between points $r$ and $r'$: it has nothing to do with electron-electron interactions since $\chi^0$ refers to independent electrons. Only in the very simplest theories is $\chi^0$ strictly local: for example static Thomas-Fermi theory assumes slow spatial variations and takes $\chi^0 = \delta^3(\vec{r} - \vec{r}') \delta n(\vec{r})/\partial \mu(\vec{r})$. The derivation of the exact nonlocal form (1) for $\chi^0$ amounts to time-dependent perturbation theory for each independent electron orbital $i$, followed by squaring and summing over occupied states $i$ to obtain the density perturbation at $r$. The energy denominator in (1) is the standard denominator appearing in the wavefunction perturbation $\delta \psi_i$, while the matrix elements $\delta V_{ij}$ of perturbation theory are reproduced by the spatial integral in (2) acting on two of the wavefunctions in (1). Alternatively (1) can be obtained from the real-space version of Feynman diagram theory, being the retarded version of the open-bubble-diagram polarisability $\pi^0$ [16]. For the uniform electron gas, (1) is simply the space Fourier transform of the familiar bare Lindhard function.

While hydrodynamic approximations for $\chi^0$ have the correct global or large-distance behaviour, they do not obtain the correct $\vec{r} \simeq \vec{r}'$ or high-$q$ behaviour embodied in (1). Thus hydrodynamic approximations are less able to describe, for example, the detailed effects of rapid electron-density falloff at a metal surface. In due course we will introduce a quasi-local approximation for $\chi^0$ which does retain the correct short ranged behaviour.

We turn now to the response of Coulomb-interacting electrons to an externally imposed potential perturbation. The Time Dependent Hartree Approximation [15], otherwise known as the Random Phase Approximation (RPA) [16], amounts to the assumption that the electron density responds, via equation (2), not to the external potential $\delta V^{\text{ext}}$, but rather to a mean-field potential consisting of $\delta V^{\text{ext}}$ plus the Coulomb field generated by the instantaneous density distribution itself. This plausible “screening” argument entails neglect of the quantum or thermal fluctuations of the density about its average value. Equivalently, it neglects the correlations between the positions of the electrons: once an electron is discovered at $r$, its coulomb repulsion reduces the probability of finding other electrons nearby, so that the potential it feels due to the other electrons is not precisely that generated by the mean density $n(r)$.

In general, for a sufficiently weak external potential perturbation $\delta V^{\text{ext}}(r) \exp(-i\omega t)$, an interacting electron system must experience a linear
density response of form

$$\delta n(\vec{r}, t) = \exp(-i\omega t) \int \chi(\vec{r}, \vec{r}', \omega) \delta V^{ext}(\vec{r}') d^3r' .$$

(3)

The linear coefficient $\chi$ in the general case will be termed the interacting susceptibility and can be regarded as the density response at $\vec{r}$ due to a potential perturbation localised at $\vec{r}'$. The above mean-field argument then leads to the following Coulomb screening equation for $\chi$ in the RPA:

$$\chi_{rpa}(\lambda, \vec{r}, \vec{r}', \omega) = \chi_0(\vec{r}, \vec{r}', \omega) + \int \chi_0(\vec{r}, \vec{r}_1, \omega) \lambda e^2 |\vec{r}_1 - \vec{r}_2|^{-1} \chi_{rpa}(\lambda, \vec{r}_2, \vec{r}', \omega) d^3r_1 d^3r_2 .$$

(4)

Here the interaction strength parameter $\lambda$ is included for later convenience and should for the present be set to unity.

The exchange and correlation energy $E_{xc}$ can now be obtained from the interacting susceptibility $\chi$ in the following fashion. For a general inhomogeneous electronic system, $E_{xc}$ can be expressed exactly in terms of the density-fluctuation correlation function [17,18] as

$$E_{xc} = \frac{1}{2} \int \int d\lambda \int d^3r \int d^3r' e^2 |\vec{r} - \vec{r}'|^{-1} \left\{ \delta \hat{n}(\vec{r}) \delta \hat{n}(\vec{r}') >_\lambda - n(\vec{r}) \delta^3(\vec{r} - \vec{r}') \right\}$$

where $\delta \hat{n}(\vec{r}) = \hat{n}(\vec{r}, t) - n(\vec{r}, t)$ is the number-density fluctuation operator.

In the derivation of (5) it was assumed [17,18] that a $\lambda$-dependent external potential $V(\lambda, \vec{r})$ is supplied to maintain the density $n(\vec{r})$ at its fully-interacting value while the electron-electron interaction strength is varied from $\lambda = 0$ to $\lambda = 1$. Without the $\lambda$ integration, equ. (5) is clearly a contribution to the potential energy arising from the correlations (both dynamical and exchange-driven) between electron positions. The mutual avoidance of electrons also leads to a kinetic energy contribution because of the uncertainty principle, and qualitatively it is this feature which necessitates the integration over the coupling-strength $\lambda$. Formally the $\lambda$ integration is derived from a Feynman-theorem argument [17,18].

We now use a frequency integral to generate the equal-time correlation function $C(\vec{r}, \vec{r}', t = 0)$ from its time Fourier transform, and then apply the zero-temperature generalised fluctuation-dissipation theorem [19], thus obtaining

$$< \delta \hat{n}(\vec{r}) \delta \hat{n}(\vec{r}') >_\lambda = (2\pi)^{-1} \int_{-\infty}^{\infty} C(\lambda, \vec{r}, \vec{r}', \omega) d\omega$$

$$= -(\hbar/\pi) Im \int_{0}^{\infty} d\omega \chi(\lambda, \vec{r}, \vec{r}', \omega)$$

$$= -(\hbar/\pi) \int_{0}^{\infty} ds \chi(\lambda, \vec{r}, \vec{r}', is) .$$

(6)
Here $\chi(\lambda, \vec{r}, \vec{r}', \omega)$ is the exact linear response of the interacting homogeneous system (with pair potential reduced by a factor $\lambda$) to an external potential $\delta V^{\text{ext}}(\vec{r}) \exp(-i \omega t)$. $\chi$ is in general defined as in equ. (3) except for the presence of a reduced interaction strength:

$$
\delta n_\lambda(\vec{r}, t) = \exp(-i \omega t) \int \chi(\lambda, \vec{r}, \vec{r}', \omega) \delta V^{\text{ext}}(\vec{r}') d^3 r'.
$$

In (6) the frequency contour has been moved by analyticity arguments to lie up the imaginary $\omega$ axis where $\chi$ is purely real. Putting equations (5) and (6) together we have the following general exact result:

$$
E_{xc} = \frac{1}{2} \int_0^1 d \lambda \int d^3 r d^3 r' e^{2|\vec{r} - \vec{r}'|^{-1}} \times \left\{ -\hbar \pi^{-1} \int_0^\infty \chi(\lambda, \vec{r}, \vec{r}', is) ds - n(\vec{r}) \delta^3(\vec{r} - \vec{r}') \right\}
$$

This equation allows us to obtain the exchange-correlation energy of an arbitrary inhomogeneous electronic system from a knowledge of the interacting density-density response $\chi$. Essentially the same formula was introduced by Harris and Jones [20] in order to investigate the surface energy of a bounded jellium metal, the only difference being that in [20] the density was not held constant by a $\lambda$-dependent external potential, so that an extra electrostatic energy term was necessary.

In the case of independent electrons the exact susceptibility is the bare susceptibility $\chi^0$, and then, since there can be no dynamical correlations, equation (8) gives the exact exchange energy $E_x$. The exact correlation energy is then found [20] as the difference between the $xc$ energy and the exchange energy:

$$
E_c = -\frac{\hbar}{2\pi} \int_0^1 d \lambda \int d^3 r \int d^3 r' e^{2|\vec{r} - \vec{r}'|^{-1}} \int_0^\infty (\chi(\lambda, \vec{r}, \vec{r}', is) - \chi^0(\vec{r}, \vec{r}', is)) ds
$$

In the present case we use the RPA approximation for $\chi$. Thus the RPA groundstate energy of a general inhomogeneous system is defined as follows. First we obtain the bare or independent-electron susceptibility from equation (1), for the actual density $n(\vec{r})$. Then we obtain the interacting susceptibility $\chi$ within the RPA by numerically solving the screening integral equation (4), for each imaginary frequency $\omega = is$ and for each coupling strength from $\lambda = 0$ to $\lambda = 1$. Finally the groundstate $xc$ energy is obtained from (8), or equivalently the correlation energy is obtained from (9).

The energy obtained in this fashion may be termed the RPA energy of the inhomogeneous many-electron system at hand. This energy is a generalisation, for inhomogeneous systems, of the familiar RPA (ring-diagram) groundstate energy of the homogeneous electron gas [16]. It is worth stressing here that this energy does include an approximate correlation energy, even though, as discussed above, the time-dependent Hartree or RPA-screening equations neglect
the correlations between electron positions in the presence of an external disturbance. The resolution of this apparent contradiction lies in the application of the fluctuation-dissipation theorem, which relates correlations of electron positions in the absence of an external influence, to the response of electrons to the presence of a time-varying external influence. The broken symmetry in the latter case causes fluctuating density inhomogeneities to occur, and the mean-field interactions between these inhomogeneities are the origin of the nontrivial correlation function which emerges when the fluctuation-dissipation theorem is applied to the RPA linear response function. This nontrivial correlation function is in turn the origin of the van der Waals energy which we show below is inherent in the RPA treatment of the groundstate energy of inhomogeneous electronic systems.

Note that it is not being claimed that the RPA-screened Coulomb interaction between two charges contains the vdW interaction as such: the vdW interaction only emerges as a part of the correlation energy after use of the fluctuation-dissipation theorem.

3. VAN DER WAALS INTERACTIONS BETWEEN SEPARATED SYSTEMS FROM RPA CORRELATION ENERGY

In order to show that the van der Waals interaction is inherent in the inhomogeneous RPA correlation energy as described above, we now consider the RPA description of the situation shown in Figure 1.

![Figure 1](image)

**Figure 1.** Typical van der Waals situation. The heavy unbroken line represents a fictitious surface dividing three-dimensional space into two regions, $R_1$ and $R_2$. A localised charge-neutral electronic system $S_1$ lies inside $R_1$ well away from the boundary, and $S_2$ is similarly located within $R_2$. The van der Waals
part of the interaction between $S_1$ and $S_2$ is present even if there is an impenetrable barrier between the dotted lines, making electron transport between $R_1$ and $R_2$ impossible, so that $\chi^{0}_{12}$ is zero. In the general case the impenetrable barrier is of course absent.

In Figure 1, two charge-neutral systems $S_1$ and $S_2$ are separated by a large distance $R$ such that transport of electrons between $S_1$ and $S_2$ is highly improbable. We partition real space into two regions $R_1$ and $R_2$ such that $R_1$ contains $S_1$ and $R_2$ contains $S_2$, with the boundary between $R_1$ and $R_2$ well separated from both $S_1$ and $S_2$.

We now split the bare susceptibility $\chi^0(r,r',\omega)$ into spatially partitioned form:

$$\chi^0(r,r',\omega) = \chi^0_{1,1}(r,r',\omega) + \chi^0_{1,2}(r,r',\omega) + \chi^0_{2,1}(r,r',\omega) + \chi^0_{2,2}(r,r',\omega)$$  \hspace{1cm} (10)

where

$$\chi^0_{1,1} = \begin{cases} \chi^0(r,r',\omega) & \text{if } r \epsilon R_1 \text{ and } r' \epsilon R_1 \\ 0 & \text{otherwise} \end{cases}$$  \hspace{1cm} (11a)

$$\chi^0_{1,2} = \begin{cases} \chi^0(r,r',\omega) & \text{if } r \epsilon R_1 \text{ and } r' \epsilon R_2 \\ 0 & \text{otherwise} \end{cases}$$  \hspace{1cm} (11b)

and similarly for $\chi^0_{2,1}$ and $\chi^0_{2,2}$.

We seek to solve the screening equations in the case that the two neutral systems are widely separated, so that $\chi^0_{1,2}$ (at the imaginary frequencies we will be using) is exponentially small because of a tunneling barrier. In the special case that there is an impenetrable barrier separating $R_1$ and $R_2$, so that particle transport from $R_1$ to $R_2$ is impossible (see dotted lines in Fig. 1), then $\chi^0_{1,2}$ and $\chi^0_{2,1}$ can even be made exactly zero. This special case emphasises the fact that the vdW energy we are about to obtain does not depend on electron transport from $R_1$ to $R_2$, nor on the presence of electron density in the region between $S_1$ and $S_2$.

As a reference consider first the case that $R_1$ contains a neutral species $S_1$, but $R_2$ is empty. (This case corresponds to figure 1 with $S_2$ removed). Then the screening equation (4) for the interacting susceptibility $\chi^{\text{rpa}}$, which we denote $\chi_{1,1}$ in this situation, becomes

$$\chi_{1,1}(r,r',\omega) = \chi^0_{1,1}(r,r',\omega)$$

$$+ \int \chi^0_{1,1}(r_1,r_2,\omega)e^2|r_1 - r_2|^{-1}\chi_{1,1}(r_2,r',\omega)d^3r_1d^3r_2.$$  \hspace{1cm} (12)

A similar equation holds for the case that $R_1$ is empty, with (1,1) replaced by (2,2) throughout.

Now consider the full RPA screening equation (4) for the van der Waals problem, with both polarisable species $S_1$ and $S_2$ present as in Figure 1. We write
the combined interacting susceptibility as the sum of the individual interacting susceptibilities plus a correction,

$$\chi = \chi_{1,1} + \chi_{2,2} + \Delta \chi.$$  \hfill (13)

We spatially partition the Coulomb interaction \(V^c(r, r') = e^2 |r - r'|^{-1}\) and also the interacting susceptibility correction \(\Delta \chi\), as in equation (11). Then, using * to represent spatial convolution, we can write equation (4) as four separate equations, one for each of the (1,1), (1,2), (2,1) and (2,2) cases. The first two of these equations are

\[
\chi_{1,1} + \Delta \chi_{1,1} = \chi_{1,1}^0 + \left(\chi_{1,1}^0 * V^c_{1,1} + \chi_{1,2}^0 * V^c_{2,1}\right) * (\chi_{1,1} + \Delta \chi_{1,1}) \\
+ \left((\chi_{1,1}^0 * V^c_{1,2} + \chi_{1,2}^0 * V^c_{2,2}) * \Delta \chi_{2,1}\right) \\
\]  \hfill (14)

\[
\Delta \chi_{1,2} = \chi_{1,2}^0 + \left(\chi_{1,1}^0 * V^c_{1,1} + \chi_{1,2}^0 * V^c_{2,1}\right) * \Delta \chi_{1,2} \\
+ \left((\chi_{1,1}^0 * V^c_{1,2} + \chi_{1,2}^0 * V^c_{2,2}) * (\chi_{2,2} + \Delta \chi_{2,2})\right). \\
\]  \hfill (15)

Similar equations hold for \(\Delta \chi_{2,1}\) and \(\Delta \chi_{2,2}\). We assume \(\chi_{1,2}^0\) and \(\chi_{2,1}^0\) are negligible, corresponding to the vdW limit in which electron transport from \(S_1\) to \(S_2\) is exponentially suppressed. Quantities such as \(\chi_{1,2}^0 * V^c_{1,2}\) will be treated as perturbations. This is reasonable for well-separated subsystems since \(\chi_{1,1}^0\) restricts \(r\) to lie deep inside region \(R_1\) while the index 1,2 on \(V^c\) requires \(r'\) to lie in region \(R_2\) so that \(|r - r'|\) is large, making \(V^c\) small. The interacting susceptibility correction \(\Delta \chi\) is generated by switching on \((V^c_{1,2} + V^c_{2,1})\), and so all of its partitioned components \(\Delta \chi_{1,1}\), \(\Delta \chi_{1,2}\) etc are of first order in the perturbation, or smaller.

Keeping only zeroth and first-order terms in (15) we find

\[
(I - \chi_{1,1}^0 * V^c_{1,1}) * \Delta \chi_{1,2} = \chi_{1,2}^0 * V^c_{2,2} * \chi_{2,2} + 2\text{nd order}. \\
\]  \hfill (16)

Using

\[
(I - \chi_{1,1}^0 * V^c_{1,1})^{-1} * \chi_{1,1}^0 = \chi_{1,1} \\
\]  \hfill (17)

from equation (12), we can write (16) as

\[
\Delta \chi_{1,2} = \chi_{1,1} * V^c_{2,2} * \chi_{2,2} + \{2\text{nd order in } V^c_{1,2}, V^c_{2,1}\}. \\
\]  \hfill (18a)

and similarly

\[
\Delta \chi_{2,1} = \chi_{2,2} * V^c_{2,1} * \chi_{1,1} + \{2\text{nd order in } V^c_{1,2}, V^c_{2,1}\}. \\
\]  \hfill (18b)

Now expanding equation (14) to lowest nonvanishing order in \(V^c_{1,2}\) and \(V^c_{2,1}\), removing zeroth order terms by using (12) in the form \(\chi_{1,1} = \chi_{0,1}^0 + \chi_{0,1}^0 * V^c_{1,1} * \chi_{1,1}\), and then using (17) and (18b) we obtain

\[
\Delta \chi_{1,1} = \chi_{1,1} * V^c_{1,2} * \Delta \chi_{2,1} + \{\text{higher order}\} \\
\]
\[ \chi_{1,1} \ast V_{1,2} \ast \chi_{2,2} \ast V_{2,1} \ast \chi_{1,1} \]

\[ + \{\text{3rd order in } V_{1,2}^c, V_{2,1}^c\}. \] (19)

Equations (18) and (19), along with the (2,2) counterpart of (19), summarise what happens to the RPA susceptibility when we switch on the Coulomb interaction between two well-separated neutral subsystems. When used with the fluctuation-dissipation theorem and a coupling-constant integration as in (9), equations (18) and (19) give rise to a term in the correlation energy which is precisely the vdW interaction. To see this, note that the correlation energy expression (9) calls for the susceptibility \( \chi \) at reduced interaction strength \( \lambda \). Thus in (18) and (19) (but not in the explicit factor appearing in (9)) we replace \( V_{1,1}, V_{1,2} \) by \( \lambda V_{1,1}^c, V_{1,2}^c \), and similarly for \( V_{2,1}^c, V_{2,2}^c \). Note that \( \chi^0 \) is independent of \( \lambda \) and does not depend on \( V_c \) (recall that there is a single particle potential \( V(\lambda, \vec{r}) \) holding the density constant). Thus, the contribution to the correlation energy (9) which depends on \( V_{1,2}^c, V_{2,1}^c \) is

\[ \Delta E_c = -\frac{\hbar}{2\pi} \int_0^\infty ds \int_0^1 d\lambda A(\lambda, s) \] (20)

where

\[ A(\lambda, s) = \int d^3r' V_c(\vec{r}, \vec{r}') \Delta \chi(\lambda, \vec{r}, \vec{r}', is) \]

\[ = \int d^3r [V_c \ast \Delta \chi(\lambda, is)]_{\vec{r}, \vec{r}' = Tr[V_c \ast \Delta \chi(\lambda, is)]] (21) \]

where the trace is defined with respect to integration over \( r \), and has the usual cyclic property. Expanding with respect to the spatial partitioning introduced earlier we have

\[ A(\lambda, s) = Tr[V_{1,1}^c \ast \Delta \chi_{1,1}(\lambda, is)] + Tr[V_{1,2}^c \ast \Delta \chi_{2,1}(\lambda, is)] \]

\[ + Tr[V_{2,1}^c \ast \Delta \chi_{1,2}(\lambda, is)] + Tr[V_{2,2}^c \ast \Delta \chi_{2,2}(\lambda, is)] \]

\[ = A_{1,1} + A_{1,2} + A_{2,1} + A_{2,2} \] (22)

Here, from (19) followed by permutation of the last factor to the front,

\[ A_{1,1} = Tr[V_{1,1}^c \ast \chi_{1,1}(\lambda, is) \ast \lambda V_{1,2}^c \ast \chi_{2,2}(\lambda, is) \ast \lambda V_{2,1}^c \ast \chi_{1,1}(\lambda, is)] \]

\[ = \lambda^2 Tr[\chi_{1,1} \ast V_{1,1}^c \ast \chi_{1,1} \ast V_{1,2}^c \ast \chi_{2,2} \ast V_{2,1}^c] \] (23)

It is interesting to note that, in order to obtain all terms in (22) which are of second order in \( V_{1,2}^c, V_{2,1}^c \), we needed the second-order result in (19) but only the first-order result in (18).
Now by differentiating the operator identity $\epsilon(\lambda)^{-1} \ast \epsilon(\lambda) = I$ we can show in general that

$$\frac{\partial}{\partial \lambda}[\epsilon(\lambda)^{-1}] = -\epsilon(\lambda)^{-1} \ast \frac{\partial \epsilon}{\partial \lambda} \ast \epsilon(\lambda)^{-1}$$

(24)

and applying this to the case $\epsilon_{1,1}(\lambda) = I - \lambda \chi_{1,1}^0 \ast V_{c,1,1}$ we find

$$\frac{\partial}{\partial \lambda} \chi_{1,1}(\lambda, is) = \frac{\partial}{\partial \lambda}[\epsilon_{1,1}^{-1} \ast \chi_{1,1}^0]$$

$$= -\epsilon_{1,1}^{-1} \ast (-\chi_{1,1}^0 \ast V_{c,1,1}) \ast \epsilon_{1,1}^{-1} \ast \chi_{1,1}^0$$

$$= \chi_{1,1} \ast V_{c,1,1}^c \ast \chi_{1,1}$$

(25)

which reproduces the first three operators in (23). Putting (25) into (23) and working similarly with $A_{2,2}$ we have

$$A_{1,1} + A_{2,2} = \lambda^2 Tr \chi_{1,1}^0 \ast V_{c,1,2}^c \ast \chi_{2,2} \ast V_{c,2,1}^c + \chi_{1,1} \ast V_{c,2,1}^c \ast \frac{\partial}{\partial \lambda}(\chi_{2,2}) \ast V_{c,2,1}^c$$

$$= \lambda^2 \frac{\partial}{\partial \lambda} Tr[V_{c,1,2}^c \ast \chi_{2,2} \ast V_{c,2,1}^c \ast \chi_{1,1}]$$

(26)

But from (22) and (18b)

$$A_{1,2} = \lambda Tr[V_{c,1,2}^c \ast \chi_{2,2} \ast V_{c,2,1}^c \ast \chi_{1,1}] = A_{2,1}.$$ 

(27)

Thus (22) becomes

$$A(\lambda, s) = (\lambda^2 \frac{\partial}{\partial \lambda} + 2\lambda) Tr[V_{c,1,2}^c \ast \chi_{2,2} \ast V_{c,2,1}^c \ast \chi_{1,1}] = \frac{\partial}{\partial \lambda}(\lambda^2 Tr[\ ]).$$

Thus the $\lambda$ integration in (20) can be done analytically, giving

$$\Delta E^c = -\hbar(2\pi)^{-1} \int d^3r d^3r' d^3r_1 d^3r_2 e^2|r - r'|^{-1} e^2|r_1 - r_2|^{-1}$$

$$\times \int_0^\infty ds \chi_{1,1}(r, r_1, is) \chi_{2,2}(r_2, r', is).$$

(28)

Here the convolutions have now been written out in full, and the susceptibilities are evaluated at the full interaction strength $\lambda = 1$. Equation (28) is the expression obtained via perturbation theory by Zaremba and Kohn [21] for the van der Waals energy between two arbitrary polarisable systems. This shows that the van der Waals interaction is contained naturally within the standard inhomogeneous RPA groundstate energy formalism. Of course, although the form of (28) is correct, the vdW energy produced by the present RPA formalism will involve the RPA susceptibilities $\chi_{1,1}$ and $\chi_{2,2}$ of the two separated systems, rather than the exact susceptibilities.
As an example of the use of equation (28) consider two point polarisable dipoles located at \( \vec{r}_0^1 \) and \( \vec{r}_0^2 \), with scalar polarisabilities \( \alpha_1(\omega) \) and \( \alpha_2(\omega) \). Under the application of an external potential \( \Phi(\vec{r}) \exp(-i\omega t) = -e^{-1}\delta V^{ext}(\vec{r}) \exp(-i\omega t) \), the dipole moment at \( r_0^1 \) is proportional to the local value of electric field:

\[
\vec{p}_1 = \alpha_1(\omega)(-\vec{\nabla} \Phi(\vec{r}_0^1)) = \alpha(\omega)e^{-1}\vec{\nabla}\delta V^{ext}(\vec{r}_0^1). \tag{29}
\]

Since a dipole moment \( p_1 \) is produced by moving an electron through a displacement \( \vec{x} = e^{-1}\vec{p}_1 \), this dipole moment can be represented in the weak-field regime by a delta-function-derivative electron number density perturbation:

\[
\delta n_1(\vec{r}, t) = \delta(\vec{r} - \vec{r}_0^1) - \delta(\vec{r} - \vec{r}_0^1 - \vec{x}/2) = -e^{-1}\vec{x}.\vec{\nabla}\delta n_1(\vec{r}, t) = +e^{-1}\vec{p}_1.\vec{\nabla}\delta n_1(\vec{r}, t)
\]

\( \simeq -e^{-1}\vec{x}.\vec{\nabla}\delta 3(\vec{r} - \vec{r}_0^1) = +e^{-1}\vec{p}_1.\vec{\nabla}\delta 3(\vec{r} - \vec{r}_0^1). \tag{30}\)

We determine the susceptibility of the isolated system \( S_1 \) by demanding that the density perturbation (30) is reproduced by the generalised response equation (3). Thus we find for a point polarisable dipole at \( r_0^1 \)

\[
\chi_{1,1}(\vec{r}, \vec{r}_1, \omega) = -e^{-2}\alpha_1(\omega)\vec{\nabla}_1.\delta 3(\vec{r} - \vec{r}_0^1)\vec{\nabla}_1.\delta 3(\vec{r}_1 - \vec{r}_0^1). \tag{31}\]

Putting (31) (plus the equivalent for \( \chi_{2,2}(\vec{r}_2, \vec{r}_2') \)) into (28) we find, with Einstein summation convention on indices \( j \) and \( k \),

\[
\Delta E_c = -\hbar(2\pi)^{-1} \int_0^\infty ds \alpha_1(is)\alpha_2(is) \times
\]

\[
\partial_j \partial_{j'} \partial_{k} \partial_{k'} |\vec{r} - \vec{r}'|^{-1}|\vec{r}_1 - \vec{r}_2|^{-1} |r=-r_2=r_0, r_1=r'=r_0 \]

\[
= -3\hbar \frac{1}{\pi R^6} \int_0^\infty ds \alpha_1(is)\alpha_2(is), \quad R = |r_0 - \vec{r}_0^2| \tag{32}\]

which is exactly the van der Waals interaction (see equ 1.18 of ref [1]).

4. QUASI-LOCAL APPROXIMATION FOR THE INDEPENDENT-ELECTRON SUSCEPTIBILITY \( \chi^0 \)

The standard local density approximation [12] for the exchange-correlation energy can be obtained by making a quasi-local approximation for the interacting susceptibility \( \chi \), as follows:

\[
\chi(\lambda, \vec{r}, \vec{r}', \omega) \simeq \chi^{LDA}(\lambda, \vec{r}, \vec{r}', \omega) = \chi^{unif}(\lambda, n = n(\vec{r}), |\vec{r} - \vec{r}'|, \omega). \tag{33}\]
Here $\chi^{unif}(\lambda, n, |\Delta\vec{r}|, \omega)$ is the susceptibility of a uniform electron gas of number density $n$. Putting the (obviously spatially unsymmetric) Ansatz (33) into (8) one readily obtains

$$E_{xc} = \int d^3r n(\vec{r}) \epsilon_{xc}(n(\vec{r}))$$

(34)

where

$$\epsilon_{xc}(n) = -N^{-1}(\hbar/2\pi) \int_0^1 d\lambda \int d^3r \int d^3r' \lambda e^2 |\vec{r} - \vec{r}'|^{-1}$$

$$\times [\int_0^\infty \chi^{unif}(\lambda, n, |\vec{r} - \vec{r}'|, is) ds - \pi \hbar^{-1} n \delta^3(\vec{r} - \vec{r}')]$$

(35)

is the exchange-correlation energy per particle of a uniform electron gas of number density $n$.

An inspection of (34) shows that the LDF approximation cannot yield the van der Waals energy of a pair of separated electron systems $S_1$ and $S_2$ as in section 3 above. Consider for example two density concentrations separated in real space by a region of zero density as imposed by an impenetrable barrier (see dotted lines in Fig. 1). Then the exchange-correlation energy from equ. (34) is the sum of the energies of the two isolated systems, there being no contribution depending on the separation because of the local character of the density dependence in (34).

The essential idea proposed here is that we should use an Ansatz like (33), not for the interacting susceptibility $\chi$, but for the bare susceptibility $\chi^0$. (It might be objected that screening is well known to reduce the effective range of response functions so that one should only make local approximations for interacting response: this is certainly true for the response $F(\vec{r}, \vec{r}')$ of the electron density at $r$ to an external point charge density at $r'$. However $\chi$, although commonly termed the “density-density response”, in fact describes the density disturbance at $r$ due to a point potential disturbance at $r'$. In this context it is noteworthy that, via the Schrodinger equation, the electron wavefunctions respond in a quasi-local manner to the local values of the potential, and not directly to the charge density which creates the potential. As a result, both $\chi$ and $\chi^0$ are more localised than $F$. $\chi$ is not more localised than $\chi^0$ in general, however, and in certain cases $\chi$ is less local than $\chi^0$: this occurs for example for real frequencies near a plasmon excitation [22], or for widely separated charge concentrations as in the classic van der Waals problem studied above. Specifically, for the system $S_1 + S_2$ studied in section 3 above, the special case with a hard wall between $R_1$ and $R_2$ has $\chi^0_{1,2} = 0$ (a kind of locality) but $\chi_{1,2} \neq 0$ (a kind of nonlocality: see eqn. (18)).

The essence of the present argument is then to presume a form of locality for $\chi^0$, allowing its values for an inhomogeneous system to be approximated from a knowledge of the bare susceptibility of a uniform electron gas. This avoids the need to calculate wavefunctions in the inhomogeneous situation. The nonlocality of the RPA-screened susceptibility $\chi$ is maintained by solving an explicitly nonlocal screening integral equation in real space.
The simplest way to attempt this approach, which is merely an approximation to RPA, is to set

$$
\chi^0(\vec{r}, \vec{r'}, \omega) \simeq \chi^0, \text{unif}(n_{av}(\vec{r}, \vec{r'}, |\vec{r} - \vec{r'}|), \omega). \tag{36}
$$

where

$$
\chi^0, \text{unif}(n, r, \omega) = (2\pi)^{-3} \int \chi^{0L}(n, k, \omega) \exp(ik \cdot \vec{r}) d^3k \tag{37}
$$

is the usual bare uniform-electron-gas Lindhard function (Feynman diagram bubble integral), Fourier-transformed into real space. The simplest form for the average density is an unsymmetrical one,

$$
n_{av}(\vec{r}, \vec{r'}) = n(\vec{r}) \tag{38}
$$

which does however have the advantage of preserving particle number as will be discussed elsewhere. One could also use a hydrodynamic approximation for $\chi^0$. This approach has been extensively investigated by Mahanty, Summerside and others [1,2,3]. To implement the hydrodynamic approach in full one has effectively to solve spatial differential equations to obtain $\chi^0$. Simple analytic results can then be obtained which are accurate for the form of the van der Waals interactions at large separation. The present method aims to work even for small separations and so must be valid both for slow and for rapid spatial variations, whereas hydrodynamics is expected to be valid only in the limit of slow variations. As will be discussed elsewhere, the present type of approximation correctly obtains some of the short-ranged, high-$q$ response properties missed by hydrodynamics, and also avoids the solution of spatial differential equations in obtaining $\chi^0$.

Note that equations (38), (36), (4) and (8) [or (9)], solved in that order, constitute a path from a chosen trial electron density $n(\vec{r})$ to an exchange and correlation energy $E_{xc}$ which we have argued will contain the van der Waals interaction, unlike the usual LDF prescription. This occurs because the nonlocal screening integral equation (4) is retained: the precise details of the nonlocal behaviour of the true $\chi^0$ which are lost in the ansatz (36) are, as we have argued, unimportant in obtaining the vdW energy. The advantage of the present approach over a full RPA xc energy calculation is that one obtains the bare susceptibility approximately from that of a uniform electron gas, without the need to find the inhomogeneous one-electron wavefunctions required as in equ. (1) for a full RPA calculation.

When the above prescription is applied to the uniform electron gas one obtains, after a little algebra, the uniform-gas correlation energy as given by diagrammatic perturbation theory in the RPA or “ring-diagram” approximation (see for example equation 12.23 of [16]). This serves to emphasise that we are dealing with an RPA type of approximation, applied in this case however to an inhomogeneous situation.

A potential problem with the above algorithm in the van der Waals context is that the Ansatz (36), (38) somewhat overestimates the bare response $\chi^{0,1,2}$ of the density in one isolated electron concentration $S_1$ to a disturbance $\delta V^{ext}$
occurring in $S_2$. For example, if $\vec{r} \in S_1$ and $\vec{r}' \in S_2$, (38) and hence (36) is nonzero even when there is a hard wall between $S_1$ and $S_2$ so that the true $\chi^0(\vec{r}, \vec{r}', \omega) = \chi^0_{1,2}$ is strictly zero. This difficulty is inevitable when the average density $n_{av}$ used in (38) depends only on $n(\vec{r})$. This is probably not a serious difficulty, however, since the spurious response $\chi^0_{1,2}^{spur}$ (which affects results mainly via the first term on the right-hand-side of equation (15)) is of Friedel form and hence is of order $|\vec{r}_1 - \vec{r}_2|^{-3}$. This spurious term competes with the right-hand side of equ. (16) which is however of order $|\vec{r}_1 - \vec{r}_2|^{-2}$ as it is formally the field due to a net-charge-neutral distribution, giving a dipole potential in leading order. Thus under a local approximation for $\chi^0$ the spurious response induced is negligible for large separations. More sophisticated quasi-local approximations, ensuring that $\chi^0_{1,2}$ is not overestimated, will be discussed elsewhere.

5. INCLUSION OF LDA-LIKE CORRELATIONS

The above theory is only an approximation to RPA, and RPA is known to yield poor exchange and correlation energies for most condensed matter systems, even though it does contain the van der Waals interaction in the case of widely-separated neutral subsystems. Here we propose a simple approximate way to remedy this by including an LDA-like local exchange and correlation term which largely avoids overcounting the RPA correlations already included.

We achieve this by adding a local-field term $F_{xc}$ to the time-dependent Hartree screening equation (4), which then becomes

\[ \chi_\lambda = \chi^0 + \chi^0 \ast (V^c + F_{xc}) \ast \chi_\lambda \]  \hspace{1cm} (39)

\[ F_{xc}(\vec{r}, \vec{r}') = \delta^3(\vec{r} - \vec{r}') \lambda^{-1} f_{xc}(\lambda^{-3} n(\vec{r})) \]  \hspace{1cm} (40)

where one possible choice for $f_{xc}$ is given for $\lambda = 1$ by

\[ f_{xc}(n) = d^2 (\epsilon_{xc}(n))/dn^2. \]  \hspace{1cm} (41)

Here $\epsilon_{xc}$ is the exchange-correlation energy per particle of a uniform electron gas of number density $n$. The choice (41) for $f_{xc}$ makes (39), for $\lambda = 1$, identical with the defining equation of the Time Dependent Local Density Approximation [23, 24] which is widely used [23, 24, 25] for the finite-frequency response of many-electron systems. To generalise this to the case of a reduced Coulomb interaction $\lambda e^2 |\vec{r} - \vec{r}'|^{-1}$ as in equation (40) we have used the following scaling argument. In a uniform zero-temperature electron gas with Coulomb coupling constant $\lambda e^2$, the relevant quantum length is $a_n^* = \lambda^{-1} \hbar^2/me^2$, the effective Bohr radius. The energy scale is $H^* = \lambda^2 me^4/\hbar^2$, the effective Hartree unit.
Thus, in a zero-temperature electron gas with density \( n \) and reduced Coulomb interaction \( \lambda V^c \), the local field term \( f_{xc} = d^2(n\epsilon_{xc})/dn^2 \) is given by

\[
\epsilon_{xc}\lambda(n) = \lambda^2 \epsilon(\lambda^{-3}n), \quad f_{xc}\lambda(n) = \lambda^{-1}f_{xc}(\lambda^{-3}n).
\]

To complete the energy functional, \( \chi(\lambda, \vec{r}, \vec{r}', \omega = is) \) from equ. (39) is then integrated with respect to \( \lambda, \omega, r \) and \( r' \) as in equ. (9), to yield \( E_c \).

This theory, when applied to the homogeneous electron gas, gives the following expression for the correlation energy per electron:

\[
\epsilon_c^n = -\hbar(2\pi)^{-4}n^{-1} \int_0^1 d\lambda \int d^3q \frac{4\pi e^2}{q^2} \int_0^\infty ds \left[ \chi(\lambda, n, q, is) - \chi^{0L}(n, q, is) \right] \]

where

\[
\chi(\lambda, n, q, is) = \chi^{0L}(n, q, is) \{ 1 - [4\pi \lambda^2 e^2 q^{-2} + \lambda^{-1}f_{xc}(\lambda^{-3}n)]\chi^{0L}(n, q, is) \}^{-1}
\]

Here \( \chi^{0L} \) is the bare Lindhard susceptibility of the uniform electron gas [16]. The quantity \( \epsilon_c^n \) from equ. (43) is not necessarily the same as the correlation part of the uniform-gas energy \( \epsilon_{xc} \) already used in the definition (41) of the static \( f_{xc} \). The basic reason for this is that we have ignored the \( q \) dependence and \( \omega \) dependence of \( f_{xc} \) corresponding to the Time Dependent Local Density Approximation. In principle if we used the \( f_{xc}(\lambda, q, \omega) \) which made (43b) the exact dynamical susceptibility of the uniform gas, then an equation similar to (43a) would of course give the exact \( \epsilon_{xc} \) for a uniform gas. We could even contemplate the use of a frequency-dependent but local approximation for the inhomogeneous-gas quantity \( f_{xc}(\lambda, \vec{r}, \vec{r}', \omega) \) (see for example the approach of Gross, Kohn and Iwamoto [26,27]) in order to carry out the present xc energy scheme. The exact \( f_{xc} \) of a uniform gas is only approximately known, however, unlike the energy \( \epsilon_{xc} \) which is known essentially exactly from Monte Carlo calculations. Probably a simpler route, if we are to avoid the inconsistency between \( \epsilon_c^n \) (equ. 43) and the input values of \( \epsilon_{xc} \), is to find a \( q \) and \( \omega \)-independent function \( f_{xc}(n) \) (not equal to \( d^2(n\epsilon_{xc})/dn^2 \)) such that the known (e.g. Monte-Carlo-derived) \( \epsilon_{xc}(n) \) of the uniform gas is reproduced by equations (43). This \( f_{xc}(n) \) function for the uniform gas could be found once and for all by solving (43), regarded as a nonlinear integral equation for the function \( f_{xc} \). This is then the “best” local frequency-independent \( f_{xc} \) for use in the present theory, in the sense that the exact uniform gas xc energy will be reproduced by the theory. Clearly such a frequency-independent \( f_{xc} \) would represent some sort of average over finite frequencies, unlike equ (41) which can be shown [28] to yield the exact static response within Kohn-Sham LDA theory. In initial tests and applications it may be simplest to use the definition (41) directly without attempting to impose a consistency condition on equ. (43), however.

6. SUMMARY
We have suggested a theory which combines elements of the RPA (highly nonlocal explicit Coulomb screening) and of local density functional theory (quasilocal approximation for the BARE inhomogeneous electron gas susceptibility, plus a local field correction). As a result, after application of the fluctuation-dissipation and Feynman theorems, it produces the van der Waals interaction in a natural fashion. The inputs to the theory are a trial inhomogeneous groundstate density $n(r)$ and a uniform-gas response quantity $f_{xc}(n)$ from equation (41) (or, preferably, from a self-consistent solution of equs. (43) with $\epsilon_{\text{xc}} = \epsilon_{\text{xc}}$). Starting from the trial $n(r)$ we form the approximate bare inhomogeneous response $\chi_0$ from (38) and (36). This $\chi_0$ then determines an inhomogeneous $\chi$ via numerical solution of the spatially inhomogeneous screening integral equation (39). The xc energy then follows from spatial, frequency, and coupling-strength integrations as in equs. (8) or (9). Equations (38), (36), (39), and (9), in that order, thus constitute a path from $n(r)$ to a correlation energy $E_c$: in this sense we have a true density functional. The energy is obtained from $n(r)$ without calculating Kohn-Sham-like orbitals. Advantages of the theory should include the ability to calculate the force between two neutral systems, yielding the van der Waals interaction at large separation and LDA-like results at small separation, while remaining well-defined and physically reasonable at intermediate separations. While our calculational procedure for the total exchange-correlation energy is more complicated than the LDA algorithm, it is certainly tractable in quasi-one-dimensional systems such as a pair of three dimensional jellium metals with a vacuum gap separating their parallel surfaces. (For this case the formalism can probably be carried out [20, 25] with the full bare response from equ. (1), thus providing a test of the local Ansatz (36) in the van der Waals context). For arbitrary three-dimensional situations the linear screening integral equation (39) is probably the time-limiting step, and since it can be expressed approximately as a matrix inversion problem it is amenable to parallel computing techniques.

One drawback of the present theory is that, for two small well-separated neutral systems, although the basic $1/R^6$ separation dependence of the Van der Waals interaction will be reproduced, the coefficient may be too large. This is because the quasilocal electron-gas estimate of the individual polarisabilities is likely to be an overestimate, being based data for a uniform gas whose energy levels are closely spaced, in contrast to the widely-spaced levels of small finite systems. This drawback should not apply to large systems such as a juxtaposed pair of metal surfaces. In this latter geometry, moreover, there already exist [29] efficient algorithms for generating suitable transforms of some of the necessary $q$-space uniform-gas quantities.

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