Gradient correction to the exchange pair-correlation function of the weighted spin-density approximation in the density functional formalism

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Received 24 June 1998; in final form 20 August 1998

Abstract

A gradient correction to the exchange pair-correlation function \( G^{\text{hom}}_{\alpha\alpha}(r_{12}) \) of the homogeneous electron gas is developed in order to improve its performance for inhomogeneous systems within the weighted spin-density approximation WSDA of density functional theory. The correction factor has the form of a Pade-type approximant of the dimensionless gradient \( \frac{4}{r^3} \ldots \). \( n_r \) is the electron spin-density and of the dimensionless argument \( k_{\alpha\alpha} \), where \( k_{\alpha\alpha} \) is the weighted spin-density Fermi momentum and \( r_{12} \) is the interelectronic distance. In the zero-gradient limit the corrected pair-correlation function reduces to \( G^{\text{hom}}_{\alpha\alpha} \), while for atoms the present WSDA with gradient correction WSDA-GC provides a substantial improvement of the calculated exchange energies compared to the standard WSDA based on \( G^{\text{hom}}_{\alpha\alpha} \).

1. Introduction

The pair-correlation function \( \overline{G}_{\alpha\alpha}(n) \) plays a key role in the density functional theory (DFT) [1,2], determining the energy \( E_{\alpha\alpha}[n] \) of exchange and correlation of a many-electron system (we use Hartree atomic units in this paper):

\[
E_{\alpha\alpha}[n] = \frac{1}{2} \int \frac{n(r_1)n(r_2)[\overline{G}_{\alpha\alpha}(r_1,r_2) - 1]}{|r_1 - r_2|} d^3r_1 d^3r_2
\]

\[
= \frac{1}{2} \int \frac{n(r_1)n(r_2)\overline{G}_{\alpha\alpha}(r_1,r_2)}{|r_1 - r_2|} d^3r_1 d^3r_2.
\]  

(1)

Here, \( n(r) \) is the electron density at \( r \) and \( \overline{G}_{\alpha\alpha} \) is the pair-correlation function integrated over the coupling parameter \( \lambda \) of the electron–electron interaction \( \lambda/|r_1 - r_2| \):

\[
\overline{G}_{\alpha\alpha}(r_1,r_2) = \int_0^1 G^{\lambda}_{\alpha\alpha}(r_1,r_2) d\lambda.
\]  

(2)

The dominant part of \( \overline{G}_{\alpha\alpha} \) is the exchange pair correlation function \( G_{\alpha\alpha}[(n)_{r_1,r_2}] \), which does not depend on \( \lambda \) and which, with its spin components \( G_{\alpha\alpha} \), yields the exchange energy \( E_{\alpha\alpha}[n_{\sigma}] \):

\[
E_{\alpha\alpha}[n_{\sigma}] = \frac{1}{2} \sum_{\sigma} \int \frac{n_{\sigma}(r_1)n_{\sigma}(r_2)G_{\alpha\alpha}(r_1,r_2)}{|r_1 - r_2|} d^3r_1 d^3r_2.
\]  

(3)
For the basic model of DFT, the exchange pair-correlation function is given with a simple analytical expression [3]

\[ G_{x_{\sigma}}(\mathbf{k}_{F\sigma}, r_{12}) = -9 \left[ \sin(\mathbf{r}_{12} \cdot \mathbf{k}_{F\sigma}) - \mathbf{r}_{12} \cdot \mathbf{k}_{F\sigma} \cos(\mathbf{r}_{12} \cdot \mathbf{k}_{F\sigma}) \right]^2 / (\mathbf{r}_{12}^2 \mathbf{k}_{F\sigma}^3), \]  

(4)

where \( \mathbf{k}_{F\sigma} = (6\pi^2 n_{\sigma})^{1/3} \) is the Fermi momentum which, together with the interelectronic distance \( r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \), forms the single dimensionless argument \( (\mathbf{k}_{F\sigma}, r_{12}) \) of \( G_{x_{\sigma}}^{\text{hom}} \). This function and the related expression of the exchange hole are used as a starting point for various DFT models and approximations for inhomogeneous systems.

In the weighted spin-density approximation (WSDA) [4–7] the functional form (4) is used in a most straightforward way and the exchange energy \( E_{\text{WSDA}}[n_{\sigma}] \) of an inhomogeneous system is calculated as follows:

\[ E_{\text{WSDA}}[n_{\sigma}] = \frac{1}{2} \sum_{\sigma} \int \int n_{\sigma}(\mathbf{r}_1) n_{\sigma}(\mathbf{r}_2) G_{x_{\sigma}}^{\text{hom}}(\mathbf{k}_{F\sigma}(\mathbf{r}_1), r_{12}) \]  

\[ \times |\mathbf{r}_1 - \mathbf{r}_2| \ d^3r_1 d^3r_2. \]  

(5)

Here, \( \mathbf{k}_{F\sigma}(\mathbf{r}_1) \) is the weighted density parameter, which for each point \( \mathbf{r}_1 \) is determined from the sum rule

\[ \int n_{\sigma}(\mathbf{r}_2) G_{x_{\sigma}}^{\text{hom}}(\mathbf{k}_{F\sigma}(\mathbf{r}_1), r_{12}) d^3r_2 = -1 \]  

(6)

to preserve the unit charge of the exchange hole. Through \( \mathbf{k}_{F\sigma}(\mathbf{r}_1) \) some information on inhomogeneity is introduced into the WSDA pair-correlation function \( G_{x_{\sigma}}^{\text{hom}}(\mathbf{k}_{F\sigma}(\mathbf{r}_1), r_{12}) \), whereas in the limit of weak inhomogeneity \( G_{x_{\sigma}}^{\text{hom}}(\mathbf{k}_{F\sigma}(\mathbf{r}_1), r_{12}) \) reduces properly to the function (4).

Atomic calculations [7,8] show that, although the WSDA with the formula (5) provides an improvement over the popular local spin-density approximation (LSDA) for the lightest atoms, it fails to do so for the heavier ones. While LSDA underestimates atomic exchange energies, WSDA consistently overestimates them (See Section 3 for the corresponding numbers and for further discussion). Because of this, a different type of approximate functions \( G_{x_{\sigma}} \) and \( G_x \), the specialized exponential models, was developed within WSDA for surface [9] and bulk regions [10] of the extended systems as well as for finite systems [8,11–16]. None of these models contain the functional form (4), so (as far as exchange concerns) they all lack the exact homogeneous-gas limit.

In this Letter, an alternative approach is proposed for a general type of many-electron systems, which preserves the exact homogeneous gas asymptotics (4) of the exchange pair-correlation function and, at the same time, corrects the calculated atomic exchange energies. This is achieved by multiplying the WSDA function \( G_{x_{\sigma}}^{\text{hom}}(\mathbf{k}_{F\sigma}(\mathbf{r}_1), r_{12}) \) by a gradient correction factor. In Section 2 the gradient correction factor is presented, which is a rational function (Pade-type approximant) of the WSDA dimensionless argument \( (\mathbf{k}_{F\sigma}(\mathbf{r}_1), r_{12}) \) and the density gradient dimensionless argument \( x_{\sigma}(\mathbf{r}_1) \) [17]

\[ x_{\sigma}(\mathbf{r}_1) = \frac{[\nabla n_{\sigma}(\mathbf{r}_1)]}{n_{\sigma}(\mathbf{r}_1)}. \]  

(7)

The latter argument is commonly used in the generalized gradient approximation (GGA) for the exchange functional [18–21]. However, in the present study it carries out a different purpose. Indeed, in GGA the gradient corrections are added to the LSDA energy density to increase the exchange energy. In contrast, in the WSDA one has to apply gradient corrections to the pair-correlation function in order to decrease the calculated exchange energy. In Section 3 the effect of the gradient correction on the form of the WSDA pair-correlation function is discussed. Exchange energies calculated for closed- and open-shell atoms of the second, third and fourth periods are compared with those calculated by the standard WSDA (Eq. (5)) as well as by LSDA and GGA.

2. Gradient corrected pair-correlation function

To introduce the gradient correction to the pair-correlation function \( G_{x_{\sigma}}^{\text{hom}}(\mathbf{k}_{F\sigma}(\mathbf{r}_1), r_{12}) \) of WSDA, we multiply it by the gradient-dependent correction fac-
The presence of the gradient parameter $f_\sigma(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1))$, thus having for the WSDA-GC function the expression

$$G_{x_\sigma}^{\text{WSDA-GC}}(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1)) = G_{x_\sigma}^{\text{hom}}(\vec{k}_{F\sigma}(r_1)r_{12},f_\sigma(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1))).$$

(8)

For the factor $f_\sigma$ the following form is chosen:

$$f_\sigma(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1)) = 1 - \frac{a(\vec{k}_{F\sigma}(r_1)r_{12})^{3/2}}{1 + b(\vec{k}_{F\sigma}(r_1)r_{12})^{3/2}} x_\sigma^2(r_1)$$

(9)

with the second term being the $[1/1]$-Padé-type rational function [22,23] of degrees 1 and 1 with respect to the WSDA dimensionless argument $(\vec{k}_{F\sigma}(r_1)r_{12})^{3/2}$ and $[2/4]$-function with respect to the dimensionless gradient argument $x_\sigma(r_1)$ (Eq. (7)). The latter argument is a parameter reflecting the local inhomogeneity of the density at $r_1$, while the former one is introduced in order to modify the form of the pair-correlation function for inhomogeneous systems. The constants $a$ and $b$ will be determined latter. The weighted density parameter $\vec{k}_{F\sigma}(r_1)$ in Eqs. (8) and (9) is calculated for each point $r_1$ as usual in the WSDA from the sum rule

$$\int n_\sigma(\vec{r}_2)G_{x_\sigma}^{\text{WSDA-GC}}(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1))d^3r_2 = -1$$

(10)

and the exchange energy is calculated from the densities $n_\sigma(\vec{r}_1)$ and $n_\sigma(\vec{r}_3)$

$$E_x = \frac{1}{2} \sum_\sigma \int \int \frac{n_\sigma(\vec{r}_1)n_\sigma(\vec{r}_2)G_{x_\sigma}^{\text{WSDA-GC}}(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1))}{|\vec{r}_1 - \vec{r}_2|}$$

$$\times d^3\vec{r}_1 d^3\vec{r}_2.$$  

(11)

Thus, the present gradient-corrected WSDA can be considered as a strict WSDA scheme.

The form of the Padé-type approximant in (9) is chosen to satisfy boundary and asymptotic properties of the exact pair-correlation function as well as some additional conditions, which we shall consider, discussing the rational function term by term. The presence of the gradient parameter $x_\sigma(r_1)$ in the numerator ensures the exact homogeneous-gas limit, that is

$$G_{x_\sigma}^{\text{WSDA-GC}}(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1) = 0) = G_{x_\sigma}^{\text{hom}}(k_{F\sigma} r_{12}).$$

(12)

The second power $x_\sigma^2(r_1)$ of the gradient argument represents the lowest-order gradient correction [24]. The presence of the WSDA argument $(\vec{k}_{F\sigma}(r_1)r_{12})$ in the numerator ensures that the function (8) has the correct unit value at zero interelectronic distance

$$G_{x_\sigma}^{\text{WSDA-GC}}(r_{12} = 0) = -1.$$  

(13)

It also provides precise cancellation of the self-interaction for an arbitrary spin-compensated two-electron system, which is a characteristic feature of WSDA. Indeed, in this case the sum rule (10) requires $\vec{k}_{F\sigma}(r_1) = 0$ for all $r_1$, so that both $f_\sigma(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1))$ and $G_{x_\sigma}^{\text{WSDA-GC}}(\vec{k}_{F\sigma}(r_1)r_{12},x_\sigma(r_1))$ have absolute values of one everywhere and the exchange energy (11) is correctly equal to minus one half of the electrostatic electron interaction energy (self-interaction). The power 3/2 of the argument $(\vec{k}_{F\sigma}(r_1)r_{12})$ is chosen to satisfy the two following conditions: First, the pair-correlation function (8) should have the proper zero derivative at zero interelectronic distance

$$\frac{\partial G_{x_\sigma}^{\text{WSDA-GC}}(r_{12})}{\partial r_{12}} |_{r_{12}=0} = 0.$$  

(14)

With the form of Eq. (9) for the correction factor, the condition (14) is achieved for powers of $(\vec{k}_{F\sigma}(r_1)r_{12})$ higher than 1. On the other hand, the WSDA-GC function $G_{x_\sigma}^{\text{WSDA-GC}}(\vec{k}_{F\sigma}(r_1)r_{12})$ should be more diffuse, as a function of $r_{12}$, than the standard WSDA function $G_{x_\sigma}^{\text{hom}}(\vec{k}_{F\sigma}(r_1)r_{12})$, the latter having a Gaussian-like form in the energetically important region of short interelectronic distances. This can be achieved with the power of $(\vec{k}_{F\sigma}(r_1)r_{12})$ in (9) lower than 2. Thus, the mean value 3/2 of the abovementioned limiting values has been chosen. As a result, the exchange energy calculated with $G_{x_\sigma}^{\text{WSDA-GC}}$ is reduced in comparison with that calculated with $G_{x_\sigma}^{\text{hom}}$, and that is the main goal of the present gradient correction.

The denominator of the rational function in (9) produces a cut-off for large values of the arguments $(\vec{k}_{F\sigma}(r_1)r_{12})$ and $x_\sigma(r_1)$. The fourth power of $x_\sigma(r_1)$ in the denominator ensures that in the region of the
density tails, where \( n_r \) is small and the argument \( x = r^{-1/3} \) diverges as \( n_r^{-1/3} \), the correction factor is close to 1 and \( G^\text{WSDA-GC} \) is close to \( G^\text{hom} \). Since the latter function produces the exact Coulombic asymptotics of the potential for the exchange hole in this region, that is

\[
\int n_r(r_2) \frac{G^\text{hom}(k_r(r_1)r_{12})}{r_{12}} \, dr_2 = -\frac{1}{|r_1|},
\]

the cut-off chosen in (9) for large \( x = r^{-1/3} \) values produces a smooth approach of the WSDA-GC functional to the asymptotics (15) in the density tail region. For the cut-off required for large values of the argument \( (k_r(r_1)r_{12}) \), the same power 3/2 of this argument as in the numerator is introduced in the denominator of (9). Higher powers of \( (k_r(r_1)r_{12}) \) might produce undesirably high values of the rational function for small values of \( (k_r(r_1)r_{12}) \) and large values of \( x = r^{-1/3} \).

The parameter \( a \) in (9) governs the magnitude of the gradient correction for relatively small \( (k_r(r_1)r_{12}) \) and \( x = r^{-1/3} \) and, together with the parameter \( b \), it defines the size of the correction for large arguments. The values \( a = 0.107 \) and \( b = 0.029 \) are chosen from fitting the WSDA-GC exchange energy obtained with (11) to the available accurate exchange Hartree–Fock energies of atoms. With these parameters, the present form of the correction factor (9) ensures its positiveness for all values of \( x = r^{-1/3} \) which can be found for atoms, and arbitrary values of \( (k_r(r_1)r_{12}) \). For small gradients the positiveness of (9) is guaranteed for all physically relevant not very large values of \( (k_r(r_1)r_{12}) \), \( (k_r(r_1)r_{12})^{3/2} < 1/(0.107x^{1/3}(r_1)) \). The results of the atomic calculations will be discussed in the next section.

3. Results of atomic calculations

First, we compare the pair-correlation functions of the original WSDA, \( G^\text{WSDA} \), and of the gradient-corrected WSDA, \( G^\text{WSDA-GC} \), for the Ne atom. These have been calculated with the Hartree–Fock density [25] and are plotted in Fig. 1 as functions of the interelectronic distance \( r_{12} \) for the radial coordinate \( r_1 = 0.43 \) a.u., which corresponds to the minimal value of the gradient argument \( x = r^{-1/3} \). The corresponding difference \( G^\text{WSDA-GC} - G^\text{WSDA} \) is plotted in Fig. 2. One can see that the gradient correction, indeed, makes function (8) more diffuse than the standard WSDA one. The former function is sharper at short interelectronic distances, but it decays more slowly. In accordance with this, the corresponding difference is positive at short \( r_{12} \) and it passes through a maximum at \( r_{12} = 0.27 \) a.u. Starting from \( r_{12} = 0.55 \) a.u., it becomes negative, passes through a minimum at \( r_{12} = 0.82 \) a.u. and then increases slowly for the \( r_{12} \) values presented.

Table 1 compares the exchange energies calculated with LSDA, WSDA (with the function

![Fig. 1. Comparison of the WSDA and WSDA-GC pair correlation functions for the Ne atom for \( r_1 = 0.43 \) a.u.](image)

![Fig. 2. Difference between the WSDA-GC and WSDA pair correlation functions of Fig. 1.](image)
Table 1
Exchange energies (with the opposite sign and in a.u.) calculated from HF densities using several exchange-only density functional approximations: LSDA, standard WSDA, WSDA-GC and GGA. Hartree–Fock estimations [19,20,31] are given for comparison.

<table>
<thead>
<tr>
<th>Atom</th>
<th>LSDA</th>
<th>WSDA</th>
<th>WSDA-GC</th>
<th>GGA</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.884</td>
<td>1.026</td>
<td>1.026</td>
<td>1.025</td>
<td>1.026</td>
</tr>
<tr>
<td>Be</td>
<td>2.312</td>
<td>2.655</td>
<td>2.541</td>
<td>2.658</td>
<td>2.667</td>
</tr>
<tr>
<td>Mg</td>
<td>14.612</td>
<td>16.814</td>
<td>15.983</td>
<td>16.001</td>
<td>15.994</td>
</tr>
<tr>
<td>Al</td>
<td>16.533</td>
<td>19.020</td>
<td>18.075</td>
<td>18.065</td>
<td>18.072</td>
</tr>
<tr>
<td>P</td>
<td>20.792</td>
<td>23.853</td>
<td>22.649</td>
<td>22.621</td>
<td>22.641</td>
</tr>
<tr>
<td>Cl</td>
<td>25.352</td>
<td>29.056</td>
<td>27.568</td>
<td>27.486</td>
<td>27.517</td>
</tr>
<tr>
<td>Ar</td>
<td>27.863</td>
<td>31.888</td>
<td>30.241</td>
<td>30.153</td>
<td>30.185</td>
</tr>
<tr>
<td>K</td>
<td>30.204</td>
<td>34.559</td>
<td>32.767</td>
<td>32.649</td>
<td>32.678</td>
</tr>
<tr>
<td>Ca</td>
<td>32.591</td>
<td>37.294</td>
<td>35.355</td>
<td>35.193</td>
<td>–</td>
</tr>
<tr>
<td>Ga</td>
<td>69.297</td>
<td>78.224</td>
<td>73.700</td>
<td>73.687</td>
<td>–</td>
</tr>
<tr>
<td>Ge</td>
<td>73.040</td>
<td>82.381</td>
<td>77.581</td>
<td>77.600</td>
<td>–</td>
</tr>
<tr>
<td>As</td>
<td>76.876</td>
<td>86.630</td>
<td>81.541</td>
<td>81.607</td>
<td>81.518</td>
</tr>
<tr>
<td>Se</td>
<td>80.682</td>
<td>90.881</td>
<td>85.513</td>
<td>85.583</td>
<td>–</td>
</tr>
<tr>
<td>Br</td>
<td>84.599</td>
<td>95.235</td>
<td>89.584</td>
<td>89.673</td>
<td>–</td>
</tr>
<tr>
<td>Kr</td>
<td>88.624</td>
<td>99.693</td>
<td>93.737</td>
<td>93.871</td>
<td>93.890</td>
</tr>
</tbody>
</table>

$G_{E_{x}}^{\text{hom}}(\hat{k}_{F_{x}}(r_{1}),r_{12})$, WSDA-GC and GGA [19] for He and atoms of the second, third and fourth periods. Our intention is to compare the performance of these functionals for densities $n_{x}(r_{1})$ obtained with an exact treatment of electron exchange. Within the Kohn–Sham theory, the rigorous exchange-only method is known to be the optimized potential model (OPM) approach [26,27]. As was established in [28–30], the exchange and total atomic energies as well as the electron densities obtained with OPM are practically identical to those obtained with the Hartree–Fock (HF) method. Bearing this in mind, we have performed all calculations with HF densities [25] and have compared the calculated exchange energies with the HF ones taken from Refs. [19,20,31]. Another reason for using HF densities is that the most popular GGA exchange functional of Ref. [19] has been parametrized for these densities, and as a check of our numerical integration method we are able to reproduce precisely the GGA exchange energies from this reference with spherically averaged spin-densities for open-shell atoms. One can hope that, just as in the case of GGA, the parameters $a = 0.107$ and $b = 0.029$ of $f_{a}$ in (9), fitted for HF densities and energies, will be also applicable to the self-consistent WSDA-GC calculations.

As was mentioned in the Introduction, we observe in the table that LSDA consistently underestimates atomic exchange energies. The corresponding absolute error gradually increases with increasing atomic number: for the F atom it already approaches 1 a.u. and for the Kr atom it amounts to 5.3 a.u. On the other hand, by its construction, the WSDA based on the pair-correlation function $G_{E_{x}}^{\text{hom}}(\hat{k}_{F_{x}}(r_{1}),r_{12})$ reproduces exactly the exchange energy of the He atom. It slightly underestimates $E_{x}$ for Be, still being in excellent agreement with the corresponding HF value. However, for heavier atoms WSDA consistently overestimates exchange. As in the case of LSDA, the error of WSDA gradually increases with increasing atomic number: it approaches 1 a.u. for Al and for Kr it amounts to 5.8 a.u. One can conclude from this comparison that, in general, WSDA based on $G_{E_{x}}^{\text{hom}}(\hat{k}_{F_{x}}(r_{1}),r_{12})$ does not provide a definite improvement with respect to LSDA.

A substantial improvement of the exchange energies is achieved in GGA [19], which is well known for the high quality of its $E_{x}$ values. The corresponding error does not exceed a few hundreds of an a.u., and only for the relatively heavy As atom it becomes somewhat larger and amounts to 0.09 a.u. Thus, the GGA exchange energies can be taken as a reference for those atoms in Table 1, for which HF values are absent.

Being a strict WSDA scheme, the present WSDA-GC of Eqs. (8)–(11) reproduces precisely the exchange energy of the two-electron He atom, as was discussed in the previous section. For the Be atom WSDA-GC produces a worse value than the standard WSDA, although still much better than the corresponding LSDA value. This is understandable, since the gradient correction is designed to reduce the usual overestimation of exchange by the standard WSDA demonstrated in Table 1, and the Be atom is simply an exceptional case, for which WSDA does not overestimate exchange. Already for N the WSDA-GC produces a slightly smaller absolute error than the WSDA, and for all heavier atoms the
gradient correction produces a substantial improvement for the exchange energies of WSDA-GC as compared to the standard WSDA.

Contrary to the standard WSDA, the error of the present WSDA-GC does not increase monotonically with the atomic number. In particular, for all atoms of the third period as well as for some atoms of the fourth period the WSDA-GC energies closely approach the corresponding HF and GGA energies. Indeed, for Na and Ar (the terminal atoms of the third period) the absolute error of WSDA-GC is less than 0.06 a.u., while for Mg, Al, Si and P the error is only 0.01 a.u. or even smaller. For Ga and Ge, the analogous atoms of the fourth period, the WSDA-GC energies are close to GGA energies. While for As and Se the difference between WSDA-GC and GGA is somewhat larger, and the WSDA-GC value \( E_x = -81.541 \) a.u. for the spherical open-shell As atom agrees better with the HF value \(-81.518 \) a.u. [31] than the corresponding GGA value \(-81.607 \) a.u.

To conclude, the present WSDA-GC scheme (Eqs. (8)–(11)) provides a substantial improvement for the exchange energies as compared to LSDA for all atoms. It also corrects, to a large extent, the overestimation of the exchange energy for heavier atoms produced by the WSDA based on \( G_{\text{spin}}(\mathbf{k}, r_1, r_2) \). Actually, the present results of WSDA-GC are of a similar quality as the best results obtained by WSDA with our previous exponential model [8,16]. However, the advantage of the WSDA-GC is that it possesses the correct limit \( 12 \) for the homogeneous gas, whereas the exponential models mentioned in the Introduction lack this crucial feature. Thus, the present WSDA-GC scheme has a wider variety of potential applications, ranging from finite systems to simple metals.

Acknowledgements

Work supported by DGES (Grant PB95-0720-C02-01). O.V. Gritsenko is an Iberdrola Visiting Professor of Science and Technology at the University of Valladolid.

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