Study of interplanar binding in graphite by extended Thomas-Fermi theory

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A model of a graphite crystal is used which consists of a set of parallel slabs of positive charge immersed in an electron sea. Each slab, about 1 Å wide, contains the charge of the nucleus and five electrons per carbon atom, homogeneously distributed in the volume of the slabs. The electron density in the region between slabs is calculated from Thomas-Fermi-Dirac theory including corrections for inhomogeneity to the kinetic energy and correlation energy. Also, a calculation is reported with the electron density obtained by a minimization of the Thomas-Fermi-Dirac-Kirzhnits functional. The results are in semiquantitative agreement with empirical data.

I. INTRODUCTION

Density-functional theory has allowed a detailed interpretation of the electronic structure of many solids. In general, the study involves the solution of a set of self-consistent one-body Schrödinger equations and gives a quantitative agreement with empirical data. (A thorough review is given in the recent book by Lundqvist and March.) In view of the success of these methods, it can be questioned whether the simpler, but less accurate, Thomas-Fermi (TF) theory and its extensions are still useful. However, there are two reasons for using TF theory. In the first place, there are systems so complex that a more refined calculation may be too involved. In the second place, theories resting upon a single equation, such as the TF theory and its extensions, may give the general trend for the variation of properties which, to some extent, is lost in more detailed calculations. The paradigmatic example is the TF model of the atom.

One of the most difficult tasks of TF and related theories is the quantitative interpretation of the chemical bond. In fact, although extended TF theory is able to predict the different energy contributions (kinetic, direct electrostatic, exchange, etc.) of a many-electron system with small errors (of a few percent), it is well known that binding comes from a delicate balance between these terms, and errors may accumulate rather than cancel. Actually, examples of a quantitative success of TF theory in the prediction of bond properties are scarce, although many qualitative agreements have been reported. The first problem that appears in the TF theory of the chemical bond is that pure TF equation does not predict binding between atoms, as was rigorously proved by Teller. Furthermore, the inclusion of the local density (Dirac) correction for exchange is not enough, and gradient terms must be included. However, gradient corrections should be used carefully as they represent the first terms in a series expansion not convergent in general. On the other hand, no practical alternative has been found other than an exact treatment of the kinetic energy term, which leads again to one-body equations, thus departing from TF theory.

The calculation of the interlayer force in graphite is one of the few examples in which extended TF theory gives an accurate interpretation of the bond properties. Graphite has the unique property of having two entirely different types of interaction binding the structure. In the basal plane, the C atoms are held in a two-dimensional hexagonal lattice by strong covalent bonds. These bonds are highly directional and account for a binding energy of order 5 eV/C-atom. On the other hand, the planes are held to each other by much weaker energies, of order 0.05 eV/C-atom, which are neither covalent nor directional. Fully ab initio band-structure calculations have been performed for graphite which have obtained excellent results for the electronic charge density, but these studies did not examine the total energy of the graphite system. On the other hand, several calculations with extended TF theory have been reported and the present calculation represents a new contribution on this line.

Graphite has several advantages with respect to other systems. In the first place, there are many reliable experimental data on the structural properties of graphite available for direct comparison with theory, like x-ray diffraction, low-energy electron diffraction, neutron scattering, and hydrostatic pressure. In the second place, graphite and its intercalated compounds are materials with important practical applications. Finally, the binding between layers can be quantitatively studied with an extremely simple "jellium" model, which gives rise to equations that can be solved very easily, even analytically in some cases. This model, which is described in detail in the next section, represents a kind of theoretical laboratory for the test of different improvements to TF theory.
The purpose of the present calculation is to try to give an answer to a number of questions that arise in the comparison of two previous Thomas-Fermi (or density-functional) calculations of interplanar binding in graphite (papers by Santos and Villagrá\(^a\) and by DiVincenzo, Mele, and Holzwarth\(^b\)). Both papers used a density functional of the form

\[ U[p] = U_{TF}[p] + U_K[p] + U_{xc}[p]. \]  

(1)

Here, the first term is the usual Thomas-Fermi energy

\[ U_{TF}[p] = \int d\mathbf{r}[(3\pi^2/10m)(3/\pi)^{2/3}p^{5/3} + (8\pi)^{-1}E^2], \]  

(2)

\( \rho(r) \) being the number of electrons per unit volume and \( E(r) \) the total electric field at \( r \). The term \( U_K \) is the first gradient correction to the kinetic energy, which, as calculated by Kirzhnits,\(^c\) is

\[ U_K[p] = (4\hbar^2/72m) \int d\mathbf{r}[(\nabla\rho)^2/\rho - 6\nabla^2\rho]. \]  

(3)

The last term of (3) gives no contribution for atoms, molecules, and solids with pointlike nuclei, so that it is possible to use, instead of (3),

\[ U_K[p] = (4\hbar^2/72m) \int d\mathbf{r} \nabla \rho \nabla \rho, \]  

(3')

which is the form taken by DiVincenzo et al.\(^d\). However, in the jellium model of Santos and Villagrá,\(^e\) where the pointlike nuclei were replaced by layers of positive charge, the form (3) was used. The term \( U_{xc}[p] \) contains exchange and correlation energy. Santos and Villagrá\(^f\) neglected correlation and used for exchange the Dirac expression

\[ U_{\delta}[p] = - (3e^2/4\hbar)(3/\pi)^{1/3}p^{4/3}, \]  

(4)

while DiVincenzo et al. considered both exchange and correlation by means of the expression proposed by Hedin and Lundqvist,\(^g\) whose leading term is just (4).

Besides the form of the density functional, the methods used in the commented papers differ in the model of graphite and the procedure used to get the density. DiVincenzo et al. used a simple superposition of densities, each one calculated for an isolated layer of carbon atoms in hexagonal array, and no minimization of the functional was made. In contrast, Santos and Villagrá considered a much simpler jellium model of graphite, but calculated the density by minimizing the energy \( U_{TF}[p] + U_{\delta}[p] \) for all electrons (6 per atom), which is equivalent to solve the Thomas-Fermi-Dirac equation.

The results of both calculations are similar, but the agreement with experimental data is better in the paper by Santos and Villagrá. For instance, 4% error\(^h\) in the interlayer distance compared with 15%,\(^i\) both by defect; or 30% error\(^j\) for the compressibility against 180%,\(^k\) both by excess. The main conclusion of this comparison seems to be that minimization of the functional is rather important for the calculation of the density. The conclusion, however, is preliminary due to the difference in the models used in both papers and the fact that Santos and Villagrá neglected correlation energy. In the present paper we study the influence of both facts by performing new calculations similar to those of Santos and Villagrá but with a more elaborate graphite model (presented in Sec. II) and including correlation energy (Sec. III). In order to test the importance of a correct minimization of the functional, we have also made a calculation starting from the Thomas-Fermi-Dirac-Kirzhnits equation, which corresponds to minimizing \( U_{TF} + U_{\delta} + U_{K} \) (Sec. IV). It is worth noting that the initial purpose of the present calculation was trying to improve the early results of Santos and Villagrá rather than making a comparison with the work by DiVincenzo et al. and, actually, when that work was published, the present calculations were practically concluded. This explains why we have not used the same functional as DiVincenzo et al. for the correlation energy.

**II. MODEL OF GRAPHITE**

On a graphite crystal it is possible to consider three kinds of electrons placed at different regions of space:

1. There are electrons \( 1s \) of the carbon atoms, which are situated inside spheres centered at each nucleus, with a radius of order \( a_0/Z \sim 0.1 \AA \), \( a_0 \) being the Bohr radius and \( Z \) the atomic number (i.e., \( Z = 6 \)). These spheres are very small in comparison with distances between nuclei (1.42 \AA).

2. There are electrons of the \( \sigma \) bonds between carbon atoms in the same layer. These electrons lie in a zone, with thickness about 1 \AA, the center of which is the layer containing the nuclei.

3. The remaining, \( 2p_z \), electrons (one per atom) occupy chiefly the region halfway between layers, a zone more than 1.5 \AA wide. These are the electrons which contribute to the binding between layers and they are the only ones that we must explicitly consider in our calculation.

It is to be expected that the electron density changes quickly in the neighborhood of nuclei, but more slowly far from them. Also, we may assume that the density in the third zone considered above will change mainly in the direction normal to the layers, but it will scarcely change in the directions parallel to the layers. This is due to the fact that the distance between layers (3.5 \AA) is much larger than the distance between nearby nuclei in a layer (1.4 \AA). In this way, we arrive at a picture of a graphite crystal as a kind of metal having “ions” in the form of slabs of positive charge (with a homogeneous distribution equivalent to one elementary charge per atom) immersed in a sea of \( 2p_z \) electrons which glue the “ions.” This picture helps us understand the metallic properties of graphite more easily than the usual picture, which sees the graphite crystal as a set of planar macromolecules bound by van der Waals forces.

We will study forces between layers of graphite by considering the variation of the energy per electron of a system of parallel “ionic slabs” when the distance \( R \) between slabs changes. Our problem is just to evaluate the energy per electron, \( E(R) \), of an electron system placed at a region bounded by two parallel planes at a distance \( R \). The number of electrons per unit area in a plane agrees with the number of atoms per unit area of a graphite layer because we consider one electron per atom contributing to binding. Then, the surface density of electrons is
\( \sigma = 0.1067 \) a.u. [from now on, we will use hartree units (a.u.) such that \( \hbar = m = e = 1 \)]. Hence, the laws of electrostatics plus symmetry arguments fix the electric field in each boundary plane to be \( 2\pi \sigma = 0.6706 \) a.u. After that, we shall evaluate the electric potential at each point in the region by means of the Thomas-Fermi-Dirac equation, which also allows for the calculation of the energy of the electron system. Before doing that, we must evaluate the width of each "ionic slab" in order to specify completely the model of graphite.

The calculation of the width of an "ionic slab" rests upon the assumption that the electron density near a nucleus does not change very much in going from the free atom to graphite except that we consider atoms with structure 1s\(^2\)2s\(^2\)2p\(^3\) (4 valence electrons) instead of the ground-state structure 1s\(^2\)2s\(^2\)2p\(^2\). Then, the density around the nucleus is

\[
\rho(r) = 2 \left| \psi_{1s} \right|^2 + \left| \psi_{2s} \right|^2 + 3 \left| \psi_{2p} \right|^2 ,
\]

where \( \psi \) are the atomic wave functions averaged to spherical symmetry. We take the atomic functions to be

\[
\psi_{1s} = a \alpha^r, \quad \psi_{2s} = -b \alpha^r + c \alpha^{-r}, \quad \psi_{2p} = \alpha^r e^{-\lambda_p r} ,
\]

where the effective charges \( \lambda_i \) and the coefficients (all in a.u.) are \( \lambda_1 = 5.775, \lambda_2 = 1.505, a = 27.76, \)

\[
b = 5.378, \quad c = 3.268, \quad d = 3.209 .
\]

These functions are normalized for the volume element \( r^2 dr \) (i.e., without the factor \( 4\pi \)). Now, we consider two parallel planes, each one at a distance \( z_0 \) from the nucleus, in such a way that a net charge of 5 electrons of the atom remains between the planes and 1 electron outside. That is, we have

\[
\int_{|z|<z_0} \rho(r) d^3r = 5 ,
\]

where \( \rho(r) \) is given as above.

After a straightforward calculation we obtain \( z_0 = 1.1826 \) a.u. Therefore, the width of the "ionic slab" is \( 2z_0 \) or about 1 Å as was estimated at the beginning of this section. As the distance between "ionic slabs" was labeled \( R \), the distance between graphite layers in our model will be \( R + 2z_0 \). In the following sections we will evaluate the energy per atom as a function of the interlayer distance.

### III. Calculation from the Thomas-Fermi-Dirac Equation

We assume that the total energy of a graphene crystal is the sum of additive contributions associated, respectively, with the "ionic slabs" and the regions between slabs. The former are assumed to be a constant, which can be set equal to zero by adjusting the scale of energies. The energy associated to one of the regions between slabs is evaluated by the Thomas-Fermi method. The calculation parallels closely one presented in a paper by Santos and Villagra\(^8\) where a more crude model of graphite was used which, however, led to a very similar calculational problem. Therefore, we will not repeat the details here, and we give only a sketch of the procedure used and the results obtained.

We start with the Thomas-Fermi-Dirac (TFD) equation

\[
\frac{d^2 \phi}{dx^2} = \frac{4}{3\pi^2} \left[ 1 + \left( 1 + 2\pi^2 \phi \right)^{1/2} \right] ,
\]

where \( \phi \) is the electric potential and \( x \) a coordinate perpendicular to the layers. The problem is one dimensional due to the assumed translational invariance. That equation is solved with the boundary conditions

\[
\left. \frac{d\phi}{dx} \right|_{x=R/2} = 0, \quad \left. \frac{d\phi}{dx} \right|_{x=0} = 0.6706 \text{ a.u.} ,
\]

where \( x = R/2 \) is a point halfway between layers (there the electric field \( d\phi/dx \) is zero by symmetry); \( x = 0 \) is the boundary of an "ionic slab," in which an electric field exists as explained in Sec. II. Equation (9) with boundary conditions (10) does not have a solution when \( R > 8.1 \) a.u., a fact related to the finite radius of the atom in the TFD theory. This prevents us from calculating accurately the exfoliation energy of graphite because we would need the energy for \( R \rightarrow \infty \). We will estimate that quantity by an extrapolation procedure explained below.

Once the function \( \phi(x) \) is obtained we calculate the energy per atom through the TFD functional

\[
U_{\text{TFD}}(R) = 2\sigma^{-1} \int_0^{R/2} dx \left[ \frac{3\pi^2}{10} \left( \frac{3}{\pi} \right)^{2/3} \rho^{5/3} + (8\pi)^{-1} \right] \left( \frac{d\phi}{dx} \right)^2 - \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{4/3} ,
\]

where \( \sigma \) is the surface density of atoms in a layer and \( \rho(x) \) the electron density, which is related to the potential through Poisson's equation

\[
\frac{d^2 \phi}{dx^2} = 4\pi \rho .
\]

Note that our method of calculating the density—in particular, the second boundary condition (10)—implies that the valence electron density is not permitted to leak into the slab region.

The calculated energy is a function of the distance between graphite layers. That function does not have a minimum, which means that the TFD theory does not predict a binding between layers. A similar result was also obtained in previous calculations.\(^8\) However, a binding is predicted if we add the correction for inhomogeneity to the kinetic energy of the electrons in the form of
Kirzhnits. This correction has the following expression in our case:

$$U_K(R) = \frac{\sigma}{36} \int_0^{R/2} \rho^{-1} \left[ \frac{d\rho}{dx} \right]^2 dx - \frac{\sigma}{6} \left[ \frac{d\rho}{dx} \right]_{x=0}.$$  

(13)

When this energy is added to Eq. (12) a function is obtained which has a minimum at a distance $R_0$. The practical method to do the calculations closely parallels the one used in Ref. 8. In particular, the integrals (11) and (13) were evaluated numerically for several values of $R$, which allowed the calculation of the interlayer equilibrium distance $d_0$, and the force constant $k$ by adjusting a suitable second-order polynomial near the minimum. The calculated values are

$$d_0 \equiv R_0 + 2x_0 = 6.36 \text{ a.u.},$$

$$k \equiv [d^2(U_{TFD} + U_K)/dx^2]_{x=R_0} = 0.0023 \text{ a.u.},$$

(14)

where $d_0$ is compared with the empirical values 6.34 a.u. (Ref. 13) and 0.0019 a.u. (Ref. 12). As stated before, the calculation of the exfoliation energy of graphite in TF theory is ambiguous. We might estimate it from the difference between the TFD energy at the minimum and at the largest separation between layers which gives a continuous solution to Eq. (9). The exfoliation energy estimated this way is 0.00198 a.u. to be compared with the empirical value 0.0016 a.u. The agreement is fairly good for an almost ab initio calculation of such a complex structure as a graphite crystal. [The only empirical parameters used have been the $\sigma$ bond length in graphite and the atomic wave functions of the carbon atoms (6).] We shall see later that the agreement is not as good as it seems.

A more correct procedure to calculate the relevant quantities is to do a fitting of the calculated TFD energies at different values of $R$ by means of a suitable function and, then, to obtain the quantities from that function. We have chosen the function

$$U(d) = -Ad^{-4} + Be^{-\alpha d} + C, \quad d = R + 2x_0$$

(15)

and the values obtained are reported in the first row of Table I. The agreement with empirical values is not as good as before.

Correlation energy can be included in the TF theory by adding a suitable term to the energy. We have used the Wigner expression, which, in our case, is

$$U_C(R) = -2\alpha^{-1} \int_0^{R/2} a\rho^{4/3}(1+b\rho^{1/3})^{-1} dx$$

(16)

with

$$a = 0.44(4\pi/3)^{1/3}, \quad b = 7.8(4\pi/3)^{1/3}. $$

Putting the density calculated from Eqs. (9) and (12) in Eq. (16) a numerical integration gives a term which must be added to $U_{TFD}(R)$. As it should be, we obtain a function with a deeper minimum than without correlation energy. A procedure similar to the first one explained above.

**TABLE I.** Calculated values compared with results of Refs. 8 and 10 and empirical values. Parameters $\alpha$, $A$, $B$, $C$ correspond to the best fitting of the function $U(d) = -Ad^{-4} + Be^{-\alpha d} + C$ to the calculated values between $d=4$ and 9 a.u. The equilibrium interlayer distance $d_0$, force constant $k \equiv (dU/d^2)$, and exfoliation energy per atom are calculated from that function. All quantities are given in hartree units ($\hbar = e = m = 1$). $U_{TFD}$ is the energy calculated from Thomas-Fermi-Dirac theory, $U_K$ ($U_K$) is the complete (incomplete) inhomogeneity correction to the kinetic energy in the form of Kirzhnits, and $U_C$ the correlation energy. $U_{TFDK}$ is the energy calculated from the Thomas-Fermi-Dirac-Kirzhnits theory. The first 7 rows refer to the model of graphite described in Sec. II, rows 8 to 12 refer to the intermediate model described in Sec. III, row 10 reports results of Ref. 8, row 11 reports the results of the calculation by DiVincenzo et al. (Ref. 10), and the last row reports the empirical values, taken from Refs. 13, 12, and 18, respectively, for $d_0$, $k$, and $U_0$.

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<tr>
<th></th>
<th>$\alpha$</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$d_0$</th>
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gives the following values for the interlayer distance, force constant, and exfoliation energy, $U_0$:

$$d_0 = 6.18 \text{ a.u.}, \quad k = 0.0032 \text{ a.u.},$$

$$U_0 = 0.0026 \text{ a.u.}$$  \hspace{1cm} (17)

Again, a more correct procedure is the fitting of the function (15) to the energies calculated for the different values of $R$. The parameters obtained way are given in row 3 of Table I. As we see, the correlation energy shortens the interlayer equilibrium distance by about 3% and contributes to binding by about 25%. However, the agreement with empirical values is worse than before, which seems to indicate that the excellent agreement of Eqs. (14) is somewhat accidental.

With respect to the inhomogeneity correction a problem appears with the second term of Eqs. (3) and (13). This term does not contribute in the TF theory of atoms and, more generally, when the external charges (nuclei) are considered pointlike. In our model of graphite this is not the case and, in our opinion, this term should be included. Indeed, it is quite important. In order to estimate the contribution of the term we have made also the calculations without it. The results are reported in rows 2 and 4 of Table I, where the inhomogeneity correction (3') to the kinetic energy is labeled $U_K$.

The adequacy of our model of graphite can be studied through a comparison with the "jellium" model of Ref. 8. Here we consider a graphite crystal as a set of parallel "ionic slabs" of width 1.18 a.u. immersed in an electron sea with 1 electron per carbon atom. The "jellium" model of Ref. 8 can be seen as similar, but with "ionic slabs" having zero width and the electron sea having 6 electrons per carbon atom. The results with both calculations are not too different (see Table I), which gives some justification for the model proposed. It is also possible to consider an intermediate model in which the electron sea has 4 electrons per atom. That is, we put the nuclei and the 1s electrons in the "ionic slabs" but we treat all valence electrons (4 per atom) by the Thomas-Fermi method. The width of the ionic slab can also be calculated easily by putting 2 instead of 5 electrons per atom in each "ionic slab" [see Eq. (8)]. The result is $z_0 = 0.175$ a.u. The results of the calculations with this intermediate model have also been made, and are reported in Table I.

For comparison, the results of the calculation by DiVincenzo et al.\textsuperscript{10} are also included in Table I. It can be seen that, after including correlation, our results are a little closer to theirs.

IV. CALCULATION FROM THOMAS-FERMI-DIRAC-KIRZHNITS EQUATION

In view of the influence of a correct minimization of the functional, we have also made calculations with a density obtained by a minimization of the functional that includes the Kirzhnits term (4) besides those previously included, (2) and (3). The Euler-Lagrange equation of that variational problem gives

$$\frac{\pi}{2} \left[ \frac{3 \rho^{2/3}}{\pi} \right]^{2/3} - \phi \left[ \frac{3 \rho}{\pi} \right]^{1/3} = \frac{-1}{36 \rho} \frac{d^2 \rho}{dx^2} + \frac{1}{72 \rho^2} \left( \frac{d \rho}{dx} \right)^2 = 0,$$  \hspace{1cm} (18)

which leads to a fourth-order equation when combined with Poisson's Eq. (8). As a consequence, we need two boundary conditions, instead of only one, at each boundary. We choose, besides the electric field $E$ given by Eq. (6), the density $\rho$ at the surface of each "ionic slab" and the gradient of the density halfway between slabs, this coming from symmetry considerations, i.e.,

$$\rho_0 = 0.0849, \quad \frac{d \rho}{dx} \bigg|_{x=R/2} = 0.$$  \hspace{1cm} (19)

The density $\rho_0$ is calculated by averaging the atomic density (5) on the plane $z = z_0$. In comparison with the calculation of the previous section, we see that an additional constraint is imposed by demanding continuity of the density at the surface of the "ionic slabs."

Equations (18) and (12) give rise to a fourth-order differential equation, that can be reduced to a third-order one by using the electric field modulus $E$ as variable, instead of the coordinate $x$. This equation can be integrated once and leads to

$$\frac{4\pi^3}{5} \left[ \frac{3 \rho}{\pi} \right]^{2/3} - \pi \left[ \frac{3 \rho}{\pi} \right]^{1/3} \rho^{4/3} = \frac{16\pi^3}{9} \frac{d^2 \rho}{dx^2} = \frac{1}{2} E^2 + \alpha,$$  \hspace{1cm} (20)

$\alpha$ being an integration constant. This constant cannot be determined directly from (10) and (19) because we do not know $d^2 \rho/dE^2$ at the boundaries. Then, we used a consistency condition by testing several values of $\alpha$ for each fixed $\rho_{R/2}$ until a numerical integration of (20) gives the correct $\rho_0$ [Eq. (19)] for $E_0$ [Eq. (10)]. This procedure gives numerically the density as a function of the electric field. On the other hand, the distance from the middle plane between slabs is easily obtained from

$$x = (2\pi)^{-1} \int_0^E \rho(E')^{-1} dE',$$  \hspace{1cm} (21)

which, at the end, gives numerically $\rho$ as a function of $x$. After that, the numerical evaluation of the energy from the functional is straightforward.

A difficulty appears with the choice between (3) and (3') for the gradient correction. If the energy is calculated from the functional (1) over the whole volume, including the "ionic slabs," then the second term of (3) gives no contribution, so that (3) and (3') are equivalent (except for a global constant in the energy). However, if the functional is applied only to the region outside the slabs, then the second term of (3) gives an important contribution to the energy. It seems that the first procedure is more correct and, indeed, we checked that it gives results closer to the empirical data. Without including correlation, we obtained the data reported on row 5 of Table I. With correlation energy included we got those of row 6.
It can be seen that the more complex minimization procedure described in this section does not improve the agreement with empirical data. This seems to be a consequence of the smaller freedom allowed by the additional constraint (19). Then, we tested a minimization of the functional without the first condition (19), i.e., choosing for each interlayer distance the value of $\rho_0$ that minimizes the functional. The results appear in row 7 of Table I.

The conclusion of all these calculations is that a minimization of the Thomas-Fermi-Dirac-Kirzhnits functional, giving rise to a fourth-order differential equation, is not reliable. An alternative procedure to get the density from a second-order equation that includes, nevertheless, gradient corrections is the equation derived recently by Schwinger\textsuperscript{20} and generalized by Santos and Leal\textsuperscript{21} (Another generalization has been given very recently by Englert and Schwinger\textsuperscript{22}) We hope that these equations will allow more reliable calculations of binding properties within extended TF theory and work in this direction is in progress. In any case, the results of the present calculation encourage the use of TF theory for more complex problems, like the study of intercalated graphite compounds, which has already been initiated.\textsuperscript{23}

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