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Thomas-Fermi approach to diatomic systems. I. Solution of the Thomas-Fermi and Thomas-Fermi-Dirac-Weizsäcker equations

E. K. U. Gross and R. M. Dreizler
Institut für Theoretische Physik der Universität, Frankfurt am Main, West Germany
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Analytical approximations to the solution of the Thomas-Fermi and Thomas-Fermi-Dirac-Weizsäcker equation for neutral systems are presented. The authors demonstrate in detail the quality of the solutions for one-center boundary conditions and provide an extension for two-center systems. Finally, the construction of effective single-particle potentials for diatomic systems based on the solutions obtained is discussed.

I. THEORY

A. Introduction

There are two quantities of primary interest in the discussion of diatomic systems: correlation diagrams and the atomic interaction potential.[1] Starting with the full time-independent Schrödinger equation for a diatomic system

$$H\Psi(q_1, \cdots, q_A, \vec{R}) = E\Psi(q_1, \cdots, q_A, \vec{R}), \qquad (1.1)$$

with

$$q = (\vec{r}, \sigma)$$

and

$$\begin{aligned} H &= H_N + H_e \\ &= \left(T_N + \frac{Z_1 Z_2}{R}\right) \\ &\quad + \left[\sum_i t_i - \sum_i \left(\frac{Z_1}{|\vec{r}_i - \frac{1}{2}\vec{R}|} + \frac{Z_2}{|\vec{r}_i + \frac{1}{2}\vec{R}|}\right) \right. \\ &\quad \left. + \frac{1}{2} \sum_{i \neq k} \frac{1}{|\vec{r}_i - \vec{r}_k|}\right] \end{aligned}$$

(the atomic unit system is used throughout this paper), we recall that the discussion of both quantities is based on the Born-Oppenheimer approximation[2]:

$$\Psi(q_1, \cdots, q_A, \vec{R}) = \Phi(q_1, \cdots, q_A, \vec{R})\psi_N(\vec{R}). \qquad (1.2)$$

With the solution of the electronic Schrödinger equation

$$H_e \Phi_n(\vec{q}, \vec{R}) = E_{e,n}(\vec{R})\Phi_n(\vec{q}, \vec{R}) \qquad (1.3)$$

as a function of the internuclear separation, we define the adiabatic interatomic interaction potential(s) via the relation

$$U_n(\vec{R}) = E_{e,n}(\vec{R}) - E_{e.n}(\infty) + \Delta_n(\vec{R}) - \Delta_n(\infty) + Z_1 Z_2/R, \qquad (1.4)$$

The correction term for the nuclear kinetic-energy operator,

$$\Delta_n(\vec{R}) = \int d\tau\, \Phi_n^*(\vec{q}, \vec{R}) T_N \Phi_n(\vec{q}, \vec{R}), \qquad (1.5)$$

is in general small and frequently omitted from consideration.

The discussion of correlation diagrams calls for a further approximation. The potential term of the electronic Schrödinger equation is supposed to be well represented in terms of an effective single-particle potential

$$H_e \to \sum_i h_i = \sum_i [t_i + v_{\text{eff}}(q_i, \vec{R})], \qquad (1.6)$$

where the local form indicated in the equation is not a necessity. It is then possible to consider the variation of the orbital energies $\epsilon_i(\vec{R})$ as a function of the internuclear separation,

$$h\varphi_i(q, \vec{R}) = \epsilon_i(\vec{R})\varphi_i(q, \vec{R}), \qquad (1.7)$$

as a general guide for both molecular structure aspects as well as atom-atom or ion-atom scattering problems.

The effective potential v_{eff} is optimally determined in the Hartree-Fock (HF) approximation. In this approximation the ground-state energy of the electronic Hamiltonian is given by

$$\begin{aligned} E_{e,0}^{\text{HF}}(\vec{R}) &= \text{Tr}_\sigma \iint d\tau\, d\tau'\, \delta(\vec{r} - \vec{r}')(-\tfrac{1}{2}\Delta)\rho(q, q') \\ &\quad + \int d\tau\, \rho(\vec{r})[W(\vec{r}) + \tfrac{1}{2}V_e(\vec{r})] - \tfrac{1}{2}\text{Tr}_\sigma \iint d\tau\, d\tau'\, \rho(q, q')\rho(q', q)\frac{1}{|\vec{r} - \vec{r}'|}, \end{aligned} \qquad (1.8)$$

with the Coulomb potential of the nuclei given by

$$W(\vec{r}) = -Z_1/|\vec{r}-\tfrac{1}{2}\vec{R}| - Z_2/|\vec{r}+\tfrac{1}{2}\vec{R}| \tag{1.9a}$$

and the electronic potential by

$$V_e(\vec{r}) = \int d\tau' \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}. \tag{1.9b}$$

The one-particle density matrix is defined as

$$\rho(q,q') = \sum_{i(\mathrm{occ})} \varphi_i^*(q',\vec{R})\varphi_i(q,\vec{R})$$

and

$$\rho(\vec{r}) = \mathrm{Tr}_\sigma \rho(\vec{r},\sigma;\vec{r},\sigma'). \tag{1.10}$$

The effective single-particle problem (1.7) for the determination of the molecular orbitals φ_i has the form

$$\begin{aligned} h\varphi(q,\vec{R}) &= [t + W(\vec{r}) + V_e(\vec{r})]\varphi(q,\vec{R}) \\ &\quad - \mathrm{Tr}_{\sigma'} \int d\tau' \frac{\rho(q,q')}{|\vec{r}-\vec{r}'|}\varphi(q',\vec{R}) \\ &= \epsilon(\vec{R})\varphi(q,\vec{R}). \end{aligned} \tag{1.11}$$

In atomic and solid-state calculations the nonlocal exchange term is often replaced by the local Slater (HFS) approximation

$$-\mathrm{Tr}_{\sigma'} \int d\tau' \frac{\rho(q,q')}{|\vec{r}-\vec{r}'|}\varphi(q',\vec{R}) \to$$

$$V_x(\vec{r},\vec{R})\varphi(q,\vec{R}), \tag{1.12}$$

with

$$V_x(\vec{r},\vec{R}) = -c[(3/\pi)\rho(\vec{r},\vec{R})]^{1/3}.$$

In Slater's original work[3] the averaging procedure is carried through after variation leading to a factor $c=\frac{3}{2}$. In later discussions[4] a value of $c=1$ was proposed. This factor arises as a consequence of averaging before variation in both the functional formalism of Kohn *et al.*[5,6] and in the direct derivation of the Thomas-Fermi-Dirac (TFD) model.[7]

The technical effort involved in carrying through self-consistent calculations for two-center situations still makes it useful to search for alternatives to a fully self-consistent scheme which provide comparable results. One possible alternative is to be found in the Thomas-Fermi (TF) model,[7,8] expecially in the extended version of the Thomas-Fermi-Dirac-Weizsäcker (TFDW) approximation[9] including inhomogeneity corrections and exchange. The general Thomas-Fermi approach can be viewed as a gradient expansion[10,11] of the full one-particle density matrix $\rho(q,q')$ in terms of the one-particle density $\rho(\vec{r})$. It thus offers relative computational ease and independence of the number of particles involved, which makes it attractive in the case of heavier systems, with the possibility of systematically approaching HF results. It should prove possible to incorporate in the same systematic fashion relativistic effects[12] relevant for the structure of heavier diatomic molecules and questions of heavy-ion scattering. There are also attempts paralleling the argument of Hohenberg and Kohn[5] to go beyond the HF picture and set up pseudopotentials for the inclusion of correlation effects.

Earlier attempts[13] to mobilize the TF and TFD approximations for diatomic systems have mainly concentrated on the calculation of the one-particle density and the direct evaluation of the energy functional $E(\rho)$ [see Sec. IB] as a function of the internuclear separation. Both the absolute values of the total molecular energies and the impossibility of molecular binding stated by the theorem of Teller and Balázs[14] indicate that the TF density and its direct application in calculating the total energy from the functional $E(\rho)$ can be regarded only as a first step in molecular calculations. A second step could be the solution of the Schrödinger equation with the two-center TF potential. The corresponding total energies and the fully quantum-mechanical density

$$\rho(\vec{r}) = \sum_{i(\mathrm{occ})} \varphi_i^*(\vec{r})\varphi_i(\vec{r}) \tag{1.13}$$

then show definite improvement compared to the TF energies and densities. This was shown for the atomic case by Latter.[15] Corresponding applications to two-center systems were already initiated[16] in 1934 but have only been continued recently.[17,18]

Further improvement can be achieved by the inclusion of Weizsäcker's inhomogeneity term.[9] If both the exchange and the Weizsäcker terms are included, already the total energies calculated from the corresponding energy functional show good agreement with HF results. In particular, Teller's theorem does not hold for the TFDW model, which is emphasized by the results of the calculation of Yonei,[19] who provided the only numerical solution of the TFDW variational equation with two-center boundary conditions available so far.

Our aim is a relatively complete survey of the possibilities offered by the (general) TF approach for the discussion of diatomic systems. The program consists of the following steps.

(i) Solution of the TF and TFDW variational equations with two-center boundary conditions in order to obtain the total electrostatic potential (or, respectively, the density) for the electrons in the diatomic system.

(ii) Following the successful work of Latter[15] in the atomic case, we solve the one-particle Schrödinger equation (1.7) in the Hartree-Fock-Slater (HFS) form (1.12) with the potential (density) of step (i) in order to obtain effective molecular orbitals and correlation diagrams.

(iii) The electronic ground-state energy $E_{e,0}(\vec{R})$ or the corresponding interaction potential is then calculated by evaluating the expectation value of H_e with a Slater determinant comprising the lowest orbitals obtained in step (ii). Further molecular quantities of interest like dipole moments are to be calculated with the molecular orbitals of step 2. The program offers some scope for improvement, if this is considered necessary.

(a) The orbitals obtained in step (ii) allow the calculation of the fully quantum-mechanical density (1.13), which could be iterated upon, providing a relatively simple HFS scheme for diatomic systems. (b) The ground-state energy can be improved upon by invoking configuration mixing[20] or perturbation theory.[21]

In this paper we will be concerned in detail with the first step, the aim being an accurate and fast solution of the TF(DW) variational equations. We found that this aim could be reached best by working with an analytical *Ansatz* for the total electrostatic potential that satisfies the appropriate boundary conditions. The parameters of the *Ansatz* are determined systematically with a minimization procedure based on the evolutionary strategy of Rechenberg.[22] In order to base this procedure on a firm footing we go back first to the one-center case (Sec. II). In Sec. III, we then revisit the two-center TF problem which we discussed in a previous paper[23] in terms of a numerical solution with the aid of the relaxation procedure. We finally consider the two-center TFDW case, where contact with the results of Yonei is made. The two diatomic systems that we used for an illustration of our results are N–N and Ne–Ne. In a subsequent paper we discuss the correlation diagrams and the electronic ground-state energies.

B. Thomas-Fermi model and its extensions

The basic relation in the TF theory is the expression for the total electronic energy of a system as a functional of the electronic density ρ:

$$E_{\mathrm{TF}}=\int d\tau\,(c_1\rho^{5/3}+\rho W+\tfrac{1}{2}\rho V_e),\qquad c_1=\tfrac{3}{10}(3\pi^2)^{2/3}, \tag{1.14}$$

where W again denotes the pure Coulomb potential of the nuclei and V_e the electrostatic potential of the charge density ρ.

Variation of E with respect to ρ with the subsidiary condition of fixed particle number,

$$\delta_\rho\left(E+V_0\int\rho\,d\tau\right)=0\,, \tag{1.15}$$

yields the TF equation

$$\tfrac{5}{3}c_1\rho^{2/3}+W+V_e+V_0=0\,. \tag{1.16}$$

With the definition of the total electrostatic potential

$$V=-W-V_e \tag{1.17}$$

and the aid of Poisson's equation

$$\rho=-(1/4\pi)\Delta V_e\,, \tag{1.18}$$

Eq. (1.16) can be cast into the well-known form

$$\Delta V=\alpha(V-V_0)^{3/2},\quad \alpha=8\sqrt{2}/3\pi\,. \tag{1.19}$$

The TF potential V is usually discussed in terms of a screening function Φ, which is generally defined by the equation

$$V=-\Phi W\,. \tag{1.20}$$

For a neutral atom, where Φ can be assumed to be spherically symmetric, we are left with

$$V=\Phi(r)(Z/r)\,. \tag{1.21}$$

Insertion of this *Ansatz* into Eq. (1.19) yields (as V_0 can be shown to be zero for neutral systems) the following differential equation for Φ:

$$\Phi''/r=\alpha\sqrt{Z}(\Phi/r)^{3/2}\,, \tag{1.22a}$$

which is equivalent to the dimensionless equation

$$\Phi''(x)=\Phi(x)^{3/2}/\sqrt{x}\,,\quad x=r/\mu\,,\qquad \mu=\tfrac{1}{4}(9\pi^2/2Z)^{1/3}\,. \tag{1.22b}$$

The equation is solved for the boundary conditions

$$\Phi(\infty)=0\,, \tag{1.23a}$$

reflecting the case of a neutral atom, and

$$\Phi(0)=1, \tag{1.23b}$$

representing the existence of the pure Coulomb potential of the nucleus at $r=0$.

From Eqs. (1.22a) and (1.22b) and the boundary condition (1.23b) it is readily seen that the exact solution has the property

$$\Phi''\underset{r\to 0}{\sim}r^{-1/2}\,.$$

The TF density is related to the screening function by the equation

TABLE I. Comparison of total atomic energies for various approximations. The values for E_{TF} and E_{TFD} are calculated from the analytical expressions given in thė book by Gombás (Ref. 7). The Hartree-Fock values E_{HF} are taken from Ref. 32.

	E_{TF}	E_{TFD}	E_{TFDW} [a]	E_{TFDW} [b]	E_{TFDW} [c]	E_{HF}
N	−72.056	−77.948	...	−54.862	−54.220	−54.401
Ne	−165.62	−176.29	−128.83	−128.442	−126.347	−128.547
Ar	−652.75	−681.18	−524.91	−521.167	−518.576	−526.812
Kr	−3289.64	−3379.91	−2745.60	−2708.93	−2638.37	−2752.05
Xe	−8472.82	−8650.26	−7213.92	−7081.94	−6889.90	−7232.13

[a] Reference 28.

[b] Present calculation based on Eqs. (1.27) and (1.28) with $\lambda=\frac{1}{5}$.

[c] Same density as in b and use of the energy functional (1.27′) with $\lambda=\frac{1}{9}$.

$$\begin{aligned}\rho&=-(1/4\pi)\Delta V_e\\&=(Z/4\pi)\Delta[(\Phi-1)/r]=(Z/4\pi)(\Phi''/r)\,.\end{aligned}\tag{1.24}$$

Thus the above relation for Φ'' is equivalent to

$$\rho \underset{r\to 0}{\sim} r^{-3/2}\,.\tag{1.25}$$

The asymptotic behavior of the TF screening function is as easily proven to be[7]

$$\Phi \underset{r\to\infty}{\sim} r^{-3}\,.\tag{1.26}$$

Both features (1.25) and (1.26) clearly show the limitations of the TF model. While (1.25) corresponds to an infinite density at $r=0$, a more realistic model should give a finite density, and in place of the asymptotic behavior (1.26), we would expect an exponential decrease for a realistic atomic potential. Table I shows the total TF energies for some rare-gas atoms in comparison to the HF values. The agreement is poor. This underlines our statement in the Sec. IA that the pure TF model can only be a starting point for the calculation of atomic and molecular systems and that improvements of the model are mandatory. It is a well-documented[24] fact that the inclusion of an exchange term (known as the TFD approximation) does not lead to marked improvement of the TF model (see total energies in Table I). Feature (1.25) remains valid in this extension and, in place of the asymptotic behavior (1.26), a rather complicated cutoff behavior[25] of the density and the potential is introduced which is difficult to handle for many-center systems.

Yonei *et al.*[26-28] could show that the additional inclusion of a quantum correction to the kinetic energy (the so-called Weizsäcker term) leads to excellent results (see total energies in Table I). Furthermore Teller's theorem[14] does not hold for the TFDW model, i.e., the calculation of molecular binding energies is possible.[19]

The energy functional in the TFDW model has the form

$$\begin{aligned}E_{\mathrm{TFDW}}=\int d\tau\,\Big(&c_1\rho^{5/3}-c_2\rho^{4/3}+\rho W\\&+\tfrac{1}{2}\rho V_e+c_3(\nabla\rho)^2/\rho\Big)\,,\end{aligned}\tag{1.27}$$

with

$$c_2=\tfrac{3}{4}(3/\pi)^{1/3},\quad c_3=\tfrac{1}{8}\lambda\,.$$

In Weizsäacker's original work[9] the constant λ was equal to one. Using a gradient expansion method for the derivation of the quantum correction, Kirzhnits[10] obtained $\lambda=\frac{1}{9}$. In view of this discrepancy Yonei[19,26-28] took λ as an adjustable parameter. It turned out that the best results were achieved for $\lambda=\frac{1}{5}$. We adopt this value with the interpretation that it provides a means of adjustment for the higher-order terms of the gradient expansion. It can indeed be checked explicitly that the use of Eq. (1.27) with $\lambda=\frac{1}{5}$ gives essentially the same results for the total electronic energies as the extended TFDW energy functional with $\lambda=\frac{1}{9}$, which was recalculated by Hodges[11] in the form

$$\begin{aligned}E^{\mathrm{ext}}_{\mathrm{TFDW}}=E_{\mathrm{TFDW}}+\int d\tau\,c_4\rho^{1/3}&\\\times\left[\left(\frac{\Delta\rho}{\rho}\right)^2-\frac{9}{8}\left(\frac{\Delta\rho}{\rho}\right)\left(\frac{\nabla\rho}{\rho}\right)^2+\frac{1}{3}\left(\frac{\nabla\rho}{\rho}\right)^4\right]&,\end{aligned}\tag{1.27′}$$

with

$$c_4=(3\pi^2)^{-2/3}/540\,.$$

With the help of the variational principle (1.15) we obtain from the energy functional (1.27),

$$\begin{aligned}&\tfrac{5}{3}c_1\rho^{2/3}-\tfrac{4}{3}c_2\rho^{1/3}+W+V_e\\&\quad+V_0+c_3[(\nabla\rho/\rho)^2-2(\Delta\rho/\rho)]=0\,.\end{aligned}\tag{1.28}$$

From this equation we can immediately show that the asymptotic form of the density ρ for a neutral system becomes

$$\rho\underset{r\to\infty}{\sim}(1/r^2)\exp[-(V_0/c_3)^{1/2}r]\,.\tag{1.29}$$

The argument goes as follows. In Eq. (1.28) we make the substitution $\chi^2=\rho$ which leads to the equation

$$\tfrac{5}{3}c_1\chi^{7/3}-\tfrac{4}{3}c_2\chi^{5/3}+(W+V_e+V_0)\chi=4c_3\Delta\chi\,. \tag{1.30}$$

In view of the fact that W, V_e, and χ should go to zero asymptotically, the term $V_0\chi$ is dominant on the left-hand side of Eq. (1.30). Se we are left with the asymptotic equation

$$\Delta\chi=(V_0/4c_3)\chi\,,$$

which is, under the assumption of spherical symmetry in the asymptotic region, equivalent to

$$\frac{d^2}{dr^2}(r\chi)=\frac{V_0}{4c_3}(r\chi)\,.$$

The solution is

$$(r\chi)=A\,\exp[(V_0/4c_3)^{1/2}r]\,,$$

which corresponds to Eq. (1.29).

Following the above definition of the atomic screening function we can insert (1.24) into Eq. (1.28). That way we obtain a differential equation for the screening function:

$$a_1\left(\frac{\Phi''}{r}\right)^{2/3}-a_2\left(\frac{\Phi''}{r}\right)^{1/3}+c_3\left[\left(\frac{\Phi'''}{\Phi''}-\frac{1}{r}\right)^2-2\frac{\Phi''''}{\Phi''}\right]-\left(\frac{Z\Phi}{r}-V_0\right)=0\,, \tag{1.31}$$

with

$$a_1=\tfrac{5}{3}c_1(Z/4\pi)^{2/3},\quad a_2=\tfrac{4}{3}c_2(Z/4\pi)^{1/3}\,.$$

From this equation [in contrast to the TF equations (1.22a) and (1.22b)] *no* restrictions for $\Phi''(r\to 0)$ can be derived. Thus it should be possible to solve Eq. (1.31) with the boundary condition

$$\Phi''\underset{r\to 0}{\sim} r \tag{1.32}$$

representing a *finite* density at $r=0$.

In conclusion, we want to point out again that the introduction of the quantum correction of the kinetic energy is able to achieve a definite improvement of the density (and the potential) in the asymptotic region and at the charge centers; we have an exponential decrease of the density [Eq. (1.29)] and a finite density at the nuclei.

II. ANALYTICAL APPROXIMATION TO THE TF AND TFDW ATOMIC SCREENING FUNCTIONS

A. TF screening function

Many approximations to the TF screening function can be found in the literature of the last thirty years (see Torrens[1] pp. 29–34). The various forms usually represent a compromise between the required accuracy and the analytical simplicity of the approximation. One of the most accurate but also most complicated forms is the one chosen by Latter[15]:

$$\Phi_L(x)=(1+0.027\,47x^{1/2}+1.243x-0.1486x^{3/2}+0.2302x^2+0.007\,298x^{5/2}+0.006\,944x^3)^{-1}\,. \tag{2.1}$$

This approximation has the correct asymptotic x^{-3} behavior of the TF function. The form we have chosen in our calculations is a modification of Latter's function:

$$\Phi(x)=(1+a_1x+a_2x^{3/2}+a_3x^2+a_4x^3)^{-1}\,. \tag{2.2}$$

The most significant difference between Latter's approximation and our function lies in the missing $x^{1/2}$ term. Only if this term is missing, the condition (1.25) is fulfilled which is, as mentioned above, one of the features of the *exact* TF function. For latter's function we find

$$\rho_L=(Z/4\pi)(\Phi_L''/r)\underset{r\to 0}{\sim} r^{-5/2}\,.$$

As a consequence of this behavior the energy functional (1.14) becomes infinite if ρ_L is inserted for the TF density. However, in Latter's work the TF density was not a quantity of interest, and the screening function itself is almost indistinguishable from our form. Figure 1 shows Latter's function and our function both in comparison to the exact numerical solution given by Kobayashi *et al.*[29]

For the proper determination of the parameters a_i in (2.2), we compared two different methods. The first is the minimization of the quantity

$$F=\int d\tau\,|\Delta V-\alpha V^{3/2}|$$

as a function of the parameters a_i; the second is the explicit minimization of the total energy (1.14) as a function of a_i where we insert (1.24) for the electron density. The results were, in general, very similar. However, it turned out that the function obtained by the energy minimization was extremely exact near the nucleus ($x\to 0$) and less accurate in the asymptotic region, while the minimization of the quantity F produced an approx-

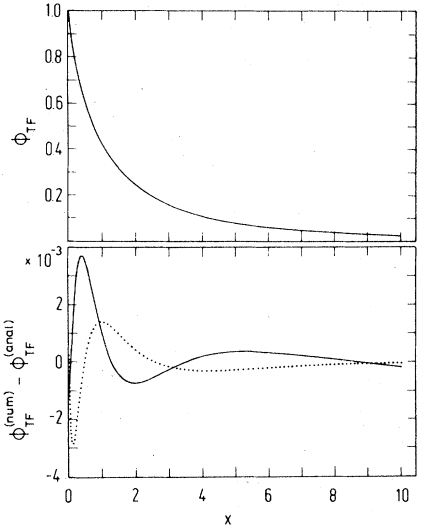

FIG. 1. Atomic TF screeing function: comparison of the analytic approximations of the present calculation (solid curve) and of Ref. 15 (dotted curve) with the exact numerical solution of Ref. 29. The lower graph shows the deviation of the analytical solutions from the numerical solution.

imation of constant quality over the whole range of x. The optimal parameter set we found was

$$a=(1.4712, -0.4973,\ 0.3875,\ 0.002\,102).$$

This is the parameter set for which the screening function is plotted in Fig. 1.

A third method for the proper determination of the parameters is the minimization of the corresponding Langrangian. This possibility, which we do not consider here, has been discussed in detail by Csavinszky.[30]

We want to point out that the direct minimization of the quantity F represents a method by which approximate analytical solutions of any differential equation can be obtained *without* the necessity of a foregoing numerical solution. Of course, the quality of the final results is very dependent on the particular choice of the analytical form. However, as long as special features of the solution like (1.25) and (1.26) and the desired boundary conditions can be included in the analytical form, very accurate results are obtained. Besides this, the final magnitude of the quantity F always represents a direct measure of the quality of the approximation.

For the numerical minimization procedures, we used an evolutionary strategy[22] with dynamical variance adjustment. This method converges very rapidly; the final parameters were reached after about 400 iterations. More details about the evolutionary strategy are given in the Appendix.

B. TFDW screening function

In this section we shall present an analytical approximation of the *atomic* TFDW screening function. For a proper choice of the analytical form we have to account for the boundary conditions (1.23a) and (1.23b) and for the relations (1.29) and (1.32) which are both features of the exact solution. Relation (1.29) can be expressed in terms of the screening function [via Eq. (1.24)]:

$$\Phi''\ \underset{r\to\infty}{\simeq}\ (1/r)\exp[-(V_0/c_3)^{1/2}r]\,. \tag{2.3}$$

We investigated functions of the form

$$\Phi=\frac{\sum_{i=0}^{n}a_i r^i}{\sum_{j=0}^{k}b_j r^j+dr^{n+1}e^{\alpha r}}\,,\quad a_0=b_0=1\,. \tag{2.4}$$

It is easily seen that all functions of this type are consistent with boundary conditions (1.23a) and (1.23b) and with the relation (2.3). In order to account for feature (1.32), the coefficients a_i, b_j, d, and α cannot be optimized independently. They must fulfill a certain relation which depends on the degree n. We tested the family of functions of the type (2.4) going up to order $n=3$ and $k=5$. The five-parameter form of order $n=1$,

$$\Phi=(1+ar)/(1+br+cr^2+dr^2e^{\alpha r})\,, \tag{2.5}$$

turned out to produce the best results. Higher orders of n or k gave no improvement or were less accurate. For this function the relation which the coefficients must fulfill is given by

$$d=b(b-a)-c\,. \tag{2.6}$$

The minimization procedures were carried out in the same fashion as for the TF function. In all cases we adopted Yonei's choice of the parameter $\lambda=\frac{1}{5}$. Table II contains the final parameters a, b, c, and α for the nitrogen atom and some rare-gas atoms. The parameter d is to be calculated from (2.6). The corresponding total energies are listed in Table I, where the results of Yonei and the present results are compared with corresponding HF values. The energies given in the column $E_{\mathrm{TFDW}}{}^{c}$ are recalculated with the same density by insertion into the extended TFDW energy functional (1.27a) with $\lambda=\frac{1}{9}$.

There is very good agreement with both Yonei's values and HF calculations for lighter atoms. For increasing Z the total atomic energies become slightly less accurate in comparison to the HF values. The simultaneous increase of the discrepancy between $E_{\mathrm{TFDW}}{}^{b}$ and $E_{\mathrm{TFDW}}{}^{c}$ indicates, that for larger Z the choice of $\lambda=\frac{1}{5}$ is less adequate, probably due to the increasing importance of higher-order terms. We plan to discuss an improvement of the approximation for heavier systems within the framework of a relativistic

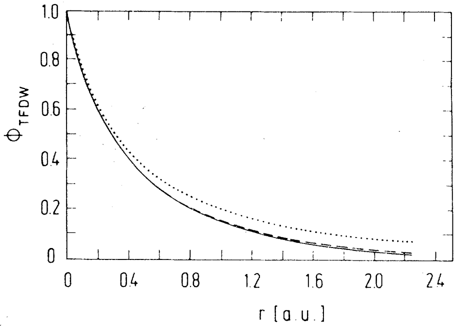

FIG. 2. Atomic TFDW screening function for neon: numerical solution of Ref. 27 (dashed curve) and analytical approximation (solid curve), in comparison to the atomic TF screening function (dotted curve).

TFDW model.

In Fig. 2 the analytical approximation of the TFDW function for Ne is compared with Yonei's result. Again the agreement is very good. The difference to the mere TF screening function which is also plotted in this figure is remarkable.

III. ANALYTICAL TWO-CENTER POTENTIALS

A. Two-center TF and TFDW potentials

In this Section we shall describe the construction of a suitable analytical approximation of the TF and TFDW potential for diatomic systems. The basic construction principle for the two-center potentials is the superposition of two spherically symmetric parts, which was first successfully applied by Hund[13] in 1932 and recently revived by Eichler and Wille[18] in the variable-screening model. We superimpose two screened Coulomb potentials

$$V=\phi_1(r_1)(Z_1/r_1)+\phi_2(r_2)(Z_2/r_2)\,, \qquad (3.1)$$

where the analytical form of the individual screening functions is given by Eq. (2.2) for the TF potential and by Eq. (2.5) for the TFDW potential, respectively. For the parameters in ϕ_1 and ϕ_2 the atomic values are no longer to be taken. Instead, the parameters must be functions of the internuclear distance R now, i.e., we optimize the parameters for each internuclear distance separately. The optimization strategy we use is still the same as described in Sec. II A.

Via the *Ansatz* (3.1), two-center boundary conditions as well as rotational symmetry with respect to the internuclear axis and the presence of the pure Coulomb potential at both charge centers are automatically satisfied. Furthermore the normalization condition

$$\int \rho\, d\tau = Z_1 + Z_2$$

TABLE II. Parameters of the atomic TFDW function for some atoms.

	α	a	b	c
N	1.3340	45.991	48.657	94.190
Ne	1.5051	73.247	76.316	182.98
Ar	1.9003	121.93	125.79	419.40
Kr	2.2778	358.69	363.70	1647.7
Xe	2.5184	581.83	587.66	3168.4

is fulfilled. This is easily seen by partial integration:

$$\int d\tau = \int\left(\frac{-1}{4\pi}\right)\Delta V_e\, d\tau$$

$$= Z_1 \int_0^\infty \phi_1''(r_1) r_1\, dr_1 + Z_2 \int_0^\infty \phi_2''(r_2) r_2\, dr_2$$

$$= Z_1 + Z_2\,.$$

In Tables III and IV the final parameters of the two-center TF potentials of Ne-Ne and N-N are listed for several internuclear distances. Figure 3 shows the analytical approximation of the two-center TF screening function in comparison to the exact numerical solution of Ref. 23. Again the agreement is excellent. In Tables V and VI the parameters of the two-center TFDW potentials of Ne-Ne and N-N are presented together with the total molecular energies. Although the precision of the total energies is better than 1% [compared with the HF results of Ref. (31)], this precision is not sufficient for the calculation of the molecu-

TABLE III. Parameters of the N-N two-center TF potential for various internuclear distances (powers of the quantity μ arising from the definition $x=r/\mu$ in (1.22b) are included in the parameters).

R	a_1	a_2	a_3	a_4
0.05	3.491	−1.0229	2.051	0.1350
0.1	3.458	−0.9865	2.030	0.1354
0.2	3.387	−0.9145	1.986	0.1380
0.3	3.288	−0.8537	1.956	0.1378
0.4	3.213	−0.8807	1.991	0.1291
0.5	3.155	−0.8999	1.991	0.1289
0.6	3.106	−0.9214	1.992	0.1287
0.7	3.102	−1.060	2.078	0.1172
0.8	3.093	−1.149	2.111	0.1154
0.9	3.110	−1.294	2.199	0.1038
1.0	3.110	−1.368	2.225	0.1021
1.1	3.112	−1.431	2.239	0.1013
1.2	3.111	−1.476	2.245	0.1010
1.3	3.115	−1.515	2.245	0.1017
1.4	3.115	−1.546	2.245	0.1001
1.5	3.122	−1.582	2.245	0.1004

lar binding energy of the N_2 molecule, which amounts to only some permillage of the total energy.

TABLE IV. Parameters of the Ne-Ne two-center TF potential for various internuclear distances (powers of the quantity μ arising from the definition $x=r/\mu$ in (1.22b) are included in the parameters).

R	a_1	a_2	a_3	a_4
0.05	3.998	−1.411	2.754	0.1714
0.1	3.959	−1.361	2.716	0.1729
0.2	3.824	−1.192	2.607	0.1793
0.3	3.693	−1.177	2.630	0.1699
0.4	3.629	−1.242	2.691	0.1512
0.5	3.584	−1.365	2.787	0.1347
0.6	3.558	−1.489	2.858	0.1251
0.7	3.528	−1.542	2.862	0.1281
0.8	3.520	−1.627	2.870	0.1324
0.9	3.503	−1.658	2.848	0.1384
1.0	3.498	−1.707	2.840	0.1415
1.1	3.492	−1.736	2.805	0.1495
1.2	3.494	−1.781	2.801	0.1499
1.3	3.488	−1.793	2.770	0.1532
1.4	3.481	−1.792	2.716	0.1638
1.5	3.478	−1.788	2.685	0.1622

B. Effective two-center single-particle potentials

In view of our final aim, the construction of a good effective single-particle potential for solving the Schrödinger equation, two modifications of the two-center potentials described in Sec. III A are mandatory: (i) The exchange term $\frac{4}{3}c_2\rho^{1/3}$ must be included as part of the effective potential, and (ii) a self-energy correction must be included for the asymptotic region in a way similar to that proposed by Latter[15] for the one-center case. Both points are taken into account by the following definition of the effective potential:

$$v_{\text{eff}}=\begin{cases}-\dfrac{Z_1\phi_1(r_1)}{r_1}-\dfrac{Z_2\phi_2(r_2)}{r_2}-c\left[\dfrac{3}{4\pi^2}\left(\dfrac{\phi_1''(r_1)Z_1}{r_1}+\dfrac{\phi_2''(r_2)Z_2}{r_2}\right)\right]^{1/3} & \text{if } |v_{\text{eff}}|>\max\left\{\dfrac{1}{r_1};\dfrac{1}{r_2}\right\}\\[2ex] -\max\left\{\dfrac{1}{r_1};\dfrac{1}{r_2}\right\} & \text{if } |v_{\text{eff}}|<\max\left\{\dfrac{1}{r_1};\dfrac{1}{r_2}\right\}.\end{cases}$$

It should be mentioned that via the inclsuion of the exchange term the potential v_{eff} (in contrast to the two-center TF and TFDW potential) cannot be split anymore into two spherically symmetric parts.

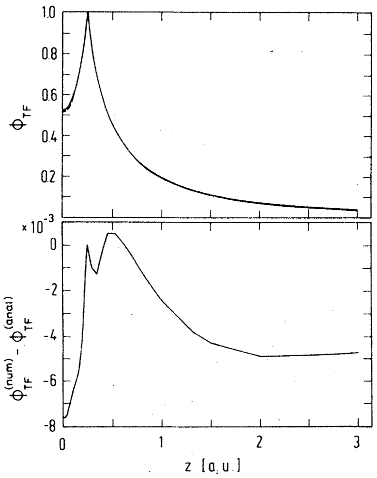

FIG. 3. Analytical approximation to the two-center TF screening function (solid curve) in comparison to the numerical solution of Ref. 23 (dashed curve). The lower graph shows the deviation of the analytical solution from the numerical solution.

IV. CONCLUSIONS

In this paper we addressed in detail the question of the solution of the TF and TFDW equations with two-center boundary conditions. We were able to show that the relatively tedious numerical procedures employed so far (as the relaxation method in the case of the TF equation) can be replaced by a semianalytical method without any loss of accuracy. The method consists in the use of a parametrized analytical *Ansatz* that incorporates the boundary and symmetry conditions of the problem. For the determination of the parameters, a fast method was found in the evolutionary strategy of Rechenberg.

It is our contention that the electron density obtained in this fashion, especially in the case of the TFDW formalism, is an excellent starting point for the consideration of further *stationary* properties of diatomic systems. The calculation of molecular orbital energies and the corresponding interaction potentials will be taken up in a sequel to this paper.

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TABLE V. Parameters of the N-N two-center TFDW potential and the corresponding total electronic energies $E_{\mathrm{TFDW}}(R)$.

R	α	a	b	c	$-E_{\mathrm{TFDW}}$[a]	$-E_{\mathrm{TFDW}}$[b]
0.05	1.4245	55.499	58.818	145.33	264.62	265.47
0.1	1.2696	42.817	46.010	98.474	245.85	247.29
0.2	1.1937	37.673	40.718	73.616	220.16	221.33
0.3	1.1769	38.184	41.138	67.779	202.93	203.62
0.4	1.1215	40.546	43.434	64.426	190.37	190.46
0.5	1.1938	40.857	43.696	69.094	180.71	180.71
0.6	1.2243	42.402	45.209	72.177	173.05	172.77
0.7	1.2715	42.858	45.636	75.697	166.80	166.47
0.8	1.2996	44.057	46.818	79.538	161.62	161.13
0.9	1.3295	44.357	47.100	81.717	157.26	156.77
1.0	1.3482	44.508	47.239	84.274	153.53	153.10
1.1	1.3766	45.322	48.043	87.143	150.31	149.81
1.2	1.3838	45.588	48.298	88.657	147.51	147.03
1.5	1.4149	45.902	48.593	92.346	140.94	140.64
1.9	1.4157	46.069	48.748	94.571	134.95	134.94
2.0	1.4099	46.143	48.820	94.867	133.78	133.84
2.068	1.4045	45.947	48.622	94.610	133.04	133.18
2.1	1.4046	45.959	48.634	94.746	132.70	132.87
2.2	1.3987	46.092	48.766	95.010	131.72	131.94
2.5	1.3833	45.909	48.579	94.729	129.20	129.67
2.75	1.3707	45.741	48.409	94.368	127.48	128.16
3.0	1.3535	45.551	48.218	93.770	126.03	126.92

[a] Based on the energy functional (1.27) with $\lambda=\frac{1}{5}$.
[b] Based on the energy functional (1.27′) with $\lambda=\frac{1}{9}$.

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APPENDIX

The evolutionary strategy provides a simple means for finding a minimum of a function $F:\mathbb{R}^n \rightarrow \mathbb{R}$. With an arbitrary start vector $x_0 \in \mathbb{R}^n$ the algorithm consists of the prescription

$$x_{\nu+1}=\begin{cases} x_\nu + z_\nu(\sigma) & \text{if } F(x_\nu + z_\nu(\sigma)) < F(x_\nu) \\ x_\nu & \text{otherwise}. \end{cases} \quad \text{(A1)}$$

TABLE VI. Parameters of the Ne-Ne two-center TFDW potential and the corresponding total electronic energies $E_{\mathrm{TFDW}}(R)$.

R	α	a	b	c	$-E_{\mathrm{TFDW}}$[a]	$-E_{\mathrm{TFDW}}$[b]
0.05	1.5630	77.090	80.861	235.24	607.42	608.39
0.1	1.5359	61.046	64.672	172.10	559.84	562.29
0.2	1.3387	59.141	62.603	137.65	497.84	498.97
0.3	1.3267	60.734	64.094	131.78	457.64	457.89
0.4	1.3611	62.587	65.880	134.56	428.90	428.59
0.5	1.3959	64.674	67.916	140.42	407.17	406.38
0.6	1.4014	67.265	70.472	145.76	390.15	388.84
0.7	1.4509	68.605	71.786	152.81	376.41	374.97
0.8	1.4858	69.273	72.430	157.67	365.12	363.72
0.9	1.5158	69.847	72.989	162.09	355.68	354.39
1.0	1.5430	71.213	74.343	167.51	347.68	346.32
1.1	1.5709	71.345	74.465	170.52	340.81	339.68
1.2	1.5971	71.945	75.056	174.34	334.86	333.86
1.3	1.6140	71.988	75.092	176.37	329.66	328.92
1.4	1.6147	71.982	75.079	177.26	325.08	324.60
1.5	1.6222	71.963	75.057	178.58	321.02	320.81
2.0	1.5754	72.633	75.712	181.47	306.08	307.05

[a] Based on the energy functional (1.27) with $\lambda=\frac{1}{5}$.
[b] Based on the energy functional (1.27′) with $\lambda=\frac{1}{9}$.

Here $z_\nu(\sigma)$ is a random vector generated from a spherically symmetric Gaussian distribution with variance σ, i.e., the probability for the random vector having the magnitude $|z|$ is given by

$$w(|z|)=(\pi 2\sigma^2)^{-n/2}\exp[-(1/2\sigma^2)z^2]\,.$$

The convergence rate of the evolutionary pattern (A1) depends much on the choice of the variance σ. If σ is not held fixed but suitably adjusted during the iteration, a marked improvement of the convergence rate can be achieved. Rechenberg[22] has found a strong criterion for the optimal choice of σ. He could show that under the assumption of spherical symmetry of F in the vicinity of the minimum, the optimum convergence rate is reached if and only if the probability of success,

$$W=\frac{A_{\text{succ}}}{A_{\text{tot}}}$$

(A_{succ} is the number of successful attempts and A_{tot} the total number of attempts), equals a critical value of $W_{\text{crit}}=0.27$. If W is greater than W_{crit}, then σ has to be increased; otherwise, σ must be decreased. As the probability of success is easily calculated during the iteration, this criterion provides a useful means for the adjustment of σ. In our calculations we controlled the probability of success after every 13th iteration and adjusted σ via the prescription

$$\sigma_{\text{new}}=\begin{cases}1.5\,\sigma_{\text{old}} & \text{if } W>W_{\text{crit}}\\ \sigma_{\text{old}}/1.5 & \text{if } W<W_{\text{crit}}\,.\end{cases}$$

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[1] For a broad review of the subject see the following books: J. Goodisman, *Diatomic Interaction Potential Energy* (Academic, New York, 1973), Vols. I and II; A. C. Hurley, *Introduction to the Electron Theory of Small Molecules* (Academic, London, 1976); I. M. Torrens, *Interatomic Potentials* (Academic, New York, 1972).

[2] M. Born and J. R. Oppenheimer, Ann. Phys. (Leipz.) 84, 457 (1927).

[3] J. C. Slater, Phys. Rev. 81, 385 (1951).

[4] O. Sinanoğlu and K. A. Brueckner, *Three Approaches to Electron Correlation in Atoms* (Yale University, New Haven, Conn., 1970).

[5] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[6] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[7] P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer, Vienna, 1949).

[8] N. H. March, *Self-consistent Fields in Atoms* (Pergamon, Oxford, 1975).

[9] C. F. von Weizsäcker, Z. Phys. 96, 431 (1935).

[10] D. A. Kirzhnits, *Field Theoretical Methods in Many-Body Systems* (Pergamon, Oxford, 1967).

[11] C. H. Hodges, Can. J. Phys. 51, 1428 (1973).

[12] D. A. Kirzhnits, Nek. Vopr. Teor. Fiz. 16, 1 (1961).

[13] F. Hund, Z. Phys. 77, 12 (1932); H. Glazer and H. Reiss, J. Chem. Phys. 21, 903 (1953); 23, 1937 (1955); J. W. Sheldon, Phys. Rev. 99, 1291 (1955); R. Townsend and G. S. Handler, J. Chem. Phys. 36, 3325 (1962); R. Townsend and J. M. Keller, *ibid.* 38, 2499 (1963); J. Goodisman, Phys. Rev. A 3, 1819 (1971); B. R. Junker and M. G. Menendez, J. Chem. Phys. 63, 1243 (1975); K. Yonei and J. Goodisman, Int. J. Quantum Chem. 11, 163 (1977); K. Yonei and J. Goodisman, J. Chem. Phys. 66, 4551 (1977).

[14] E. Teller, Rev. Mod. Phys. 34, 627 (1962); N. L. Balàzs, Phys. Rev. 156, 156 (1967).

[15] R. Latter, Phys. Rev. 99, 510 (1955).

[16] A. Recknagel, Z. Phys. 87, 375 (1934).

[17] J. Goodisman, Theor. Chim. Acta 25, 205 (1972).

[18] J. Eichler and U. Wille, Phys. Rev. Lett. 33, 56 (1974); Phys. Rev. A 11, 1973 (1975).

[19] K. Yonei, J. Phys. Soc. Jpn. 31, 882 (1971).

[20] E. W. Thulstrup and A. Anderson, J. Phys. B 8, 965 (1975).

[21] D. L. Freeman and M. Karplus, J. Chem. Phys. 64, 2641 (1976).

[22] I. Rechenberg, *Evolutionsstrategie*, *Problemata 15* (Frommann-Holzboog, Stuttgart, 1973).

[23] E. Gross and R. M. Dreizler, Phys. Lett. A 57, 131 (1976).

[24] H. M. Schey and J. L. Schwartz, Phys. Rev. 137, A709 (1965).

[25] J. C. Slater, Int. J. Quantum Chem. Symp. 9, 7 (1975).

[26] K. Yonei and Y. Tomishima, J. Phys. Soc. Jpn. 20, 1051 (1965).

[27] Y. Tomishima and K. Yonei, J. Phys. Soc. Jpn. 21, 142 (1966).

[28] K. Yonei, J. Phys. Soc. Jpn. 22, 1127 (1967).

[29] S. Kobayashi, T. Matsukuma, S. Nagai, and K. Umeda, J. Phys. Soc. Jpn. 10, 759 (1955).

[30] P. Csavinszky, Phys. Rev. 166, 53 (1968); J. Phys. Soc. Jpn. 28, 1302 (1970); Phys. Rev. A 5, 2198 (1972); 8, 1688 (1973).

[31] W. C. Ermler, R. S. Mulliken, and A. C. Wahl, J. Chem. Phys. 66, 3031 (1977).

[32] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).