

Formation of Stable Molecules within the Statistical Theory of Atoms*

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We show that no theory can describe a stable molecule or molecular ion if it expresses the charge density as a function of the electric potential alone. Such theories comprise the Thomas-Fermi, Thomas-Fermi-Dirac, Thomas-Fermi-Gombás theories. The Thomas-Fermi theory with the Fermi-Amaldi correction cannot give rise to molecular binding for homonuclear, diatomic, neutral molecules if the total number of electrons in the molecule equals or exceeds 4. The Thomas-Fermi-Weizsäcker theory gives stable homonuclear, diatomic molecules.

I. INTRODUCTION

THE Thomas-Fermi (TF) theory of atoms was also applied to molecules, crystals and metals,¹ by calculating the self-consistent electron distribution in the presence of more than one attractive center. The question arises as to whether this approximate computation is able to describe stable systems in the following sense. If the separation of the system into its atomic constituents would always lead, within the TF approximation, to a release of energy, the TF theory cannot account for stable systems. Sheldon has shown by a numerical computation that the Thomas-Fermi-Dirac (TFD) theory leads to no stable N₂ molecules. He also suggested that this may be a general property of the TFD model.²

More recently, Lee, Longmire, and Rosenbluth³ have shown that for homonuclear diatomic molecules the TF method admits no solutions which are stable. Independently, Teller⁴ demonstrated that this result holds true for any molecule both within the TF theory and the TF theory amended by Dirac to include exchange forces (TFD theory).

In this note we intend to demonstrate three things. (1) The same result holds in any theory in which the electron density is not an explicit function of the position, but varies from point to point only by virtue of its dependence on the local electric potential. Thus, if $n(x)$ is the number density of the electrons at x , and $\Phi(x)$ is the electrostatic potential at x , no binding is possible if $n(x) = f(\Phi)$, where f can be an arbitrary, non-negative function. (It is essential that n should depend on Φ only, and neither on its derivatives, nor on other functions.) Teller's theorem now immediately follows, since, for the two cases discussed, n is a simple function of Φ . Also, we find that the situation is not altered if we introduce the so-called correlation correction.⁵ (2) If we apply the Fermi-Amaldi (FA) correc-

tion,⁶ molecular binding occurs only for molecules with a total electron content less than four. (3) If we introduce the Weizsäcker correction⁷ binding will occur.

II. THE BINDING FORCE

In this section we derive the relevant results for a diatomic, homonuclear, neutral molecule. Later we shall show how we can generalize some of the results to arbitrary molecules. Instead of the energetic considerations given by Teller we shall follow Lee *et al.* and imagine the nuclei of the molecule held fixed by external forces, and investigate the internal forces acting on one of the nuclei. If this is pointed towards the other nucleus, the molecule wants to contract, and binding is present; if it points away from the other nucleus the molecule wants to fall apart; if the latter is true for all separations, no binding is possible. Here we shall not investigate the possibility that the potential of the binding force is so shallow that no quantized energy level can be accommodated in it. For the present purpose binding means: There is a range of separation such that the constituents attract each other.

Consider the diatomic molecule with nuclei A and B (see Fig. 1). Let ρ_A , ρ_B denote the (positive) charge densities of nuclei A and B , and ρ the (negative) charge density of the electrons. Sometimes we shall write $\rho = -en$, where e is positive and n is the number density of the electrons. Our aim is to find $\mathbf{F}_A = \int \rho_A \mathbf{E} dV$, which, by symmetry, can only have a component along the

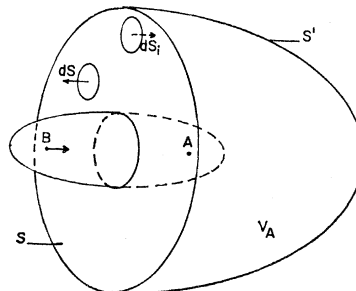


FIG. 1. Volume of integration V_A bounded by surfaces S and S' . S bissects the molecule which has its two nuclei located at B and A . S' may be at infinity. Positive direction is indicated by arrow at B .

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¹ P. Gombás, *Die Statistische Theorie des Atoms* (Springer Verlag, Vienna, 1949), p. 266.

² J. W. Sheldon, *Phys. Rev.* **99**, 1291 (1955).

³ A. R. Lee, C. L. Longmire, and M. Rosenbluth (unpublished).

⁴ E. Teller, *Rev. Mod. Phys.* **34**, 627 (1962).

⁵ Reference 1, p. 96.

⁶ Reference 1, p. 65.

⁷ Reference 1, p. 110.

line AB . Let us consider the direction from left to right, from B to A , as positive, hence a positive force on A would tend to separate A from B . From Poisson's equation $\rho_A = -(1/4\pi)\Delta\Phi - \rho - \rho_B$; multiply this by $\mathbf{E} = -\text{grad}\Phi$ and integrate over the volume V_A enclosed by S and S' , as indicated in Fig. 1. V_A contains the right half of the molecule around the nucleus A . S is a symmetry plane perpendicular to the equipotential surfaces; the S' surface encloses the molecule, and on it the electric field is zero, if the molecule is neutral. S' may have to be located at infinity. We obtain

$$\mathbf{F}_A = \frac{1}{4\pi} \int (\Delta\Phi) \text{grad}\Phi dV - \mathbf{F}. \quad (1)$$

The integral over the electron charge density gives $-\mathbf{F}$, where \mathbf{F} is the force acting on the electron cloud in V_A . ρ_B is zero in V_A ; hence it contributes nothing. Integrate on the right-hand side twice by parts. We obtain

$$\mathbf{F}_A = \frac{1}{4\pi} \int_{S+S'} \text{grad}\Phi \text{grad}\Phi \cdot d\mathbf{S} - \frac{1}{8\pi} \int_{S+S'} (\text{grad}\Phi)^2 d\mathbf{S} - \mathbf{F}, \quad (2)$$

where $d\mathbf{S}$ is the surface element of integration with the normal pointing outwards; we may also introduce $-d\mathbf{S} = d\mathbf{S}_i$, where $d\mathbf{S}_i$ has its normal inward. On S' the electric field is zero; moreover $\text{grad}\Phi$ lies in the plane S , since S is perpendicular to the equipotential surfaces. Thus the first integral contributes nothing, and the second is reduced to an integration over S .

In the integral the integrand is always positive; $d\mathbf{S}$ is a vector pointing towards B , thus, $-d\mathbf{S} = d\mathbf{S}_i$ points away from B . Hence the integral gives rise to a positive force on A , which points away from the other nucleus. This force can be interpreted as the pressure of the electric field between the nuclei arising through the Maxwell stresses. The binding will depend on the sign of \mathbf{F} ; if \mathbf{F} is negative, no binding is possible. In the force \mathbf{F} the self-force is included, which arises through the action of the charge elements within nucleus A . Consider the nucleus as a small charged sphere. Then, by symmetry this self-force is zero, as long as the surface S does not intersect the nucleus; thus the self-force part of \mathbf{F} contributes nothing as long as we do not bring the nuclei A and B so close together as to fuse them into the nucleus of a new atom. If we fuse the two nuclei together, the surface S will pass *through* this nucleus, and part of the self-force will reappear in F .⁸ Writing $\rho = -en$, our problem will then be to analyze the right-

hand side of the equation

$$\mathbf{F}_A = \frac{1}{8\pi} \int_S d\mathbf{S}_i E^2 + e \int_{V_A} dV n \mathbf{E}, \quad (3)$$

$$\mathbf{E} = -\text{grad}\Phi.$$

III. THE EVALUATION OF THE BINDING FORCE

Equation (3) is completely general; we used only Poisson's equation. To proceed further we must invoke a theory which, coupled with Poisson's equation, enables us to compute ρ and Φ . This is accomplished if we find an additional relation between ρ and Φ . The TF theory and its different extensions furnish us with such relations. In particular the TF theory, the TFD, theory, and their extensions by Gombás, including correlation effects, give a simple algebraic relation between ρ and Φ . The Fermi-Amaldi correction gives a relation between ρ , Φ , and the electrostatic potential of the nuclei; The Weizsäcker correction changes this relation between ρ and Φ into a *differential equation*.

Let us first suppose that the theory gives a relation between ρ and Φ alone, not involving the derivatives, or other functions. Write $\rho = -en$, with $n = f(\Phi)$, where, as yet, f is an arbitrary, non-negative function. Then

$$\mathbf{F} = e \int f(\Phi) \text{grad}\Phi dV = e \int dV \text{grad} \int_0^\Phi f(\Phi') d\Phi'$$

$$= e \int d\mathbf{S} \int_0^\Phi f(\Phi') d\Phi' = -e \int d\mathbf{S}_i \int_0^\Phi f(\Phi') d\Phi'. \quad (4)$$

Again, only the integration over S contributes. [This is true in spite of the arbitrary nature of f , provided (a) Poisson's equation with this $n = f(\Phi)$ has solutions with cylindrical symmetry; (b) $\int n dV$ converges if we substitute this solution Φ in $n = f(\Phi)$. (a) is needed for the first integral over S in Eq. (2) to vanish; (b) is needed for the integrals over S' in Eq. (2) to vanish. If no such solution exists there is no theory to investigate.] Now, f is a non-negative function of its argument, hence its integral is always positive, or zero, making the integrand in the surface integral positive, or zero. Since $d\mathbf{S}_i$ points in the positive direction, this makes \mathbf{F} negative. No binding is possible. From this we conclude that no theory, however complex, can describe binding, so long as within it the density can be expressed as a (local) function of the electric potential alone. In the TF theory

$$f = \sigma(\Phi - \Phi_0)^{3/2},$$

$$\sigma = (1/3\pi^2)(2/ea)^{3/2}, \quad a = \text{Bohr radius}. \quad (5)$$

For the TFD theory

$$f = \sigma[(\Phi - \Phi_0 + \tau^2)^{1/2} + \tau]^3, \quad \tau = (1/2\pi^2)^{1/2}(e/a)^{1/2}. \quad (6)$$

Φ_0 is related to the chemical potential μ of the electrons,

⁸ J. L. Schwartz [Rev. Mod. Phys. 35, 734 (1963)] pointed out that Teller's proof of his theorem seems to hold even if we fuse the two nuclei. This leads to the incorrect result that the TF atom itself is unstable. As we see, this objection does not apply to our proof of Teller's theorem.

$-e\Phi_0 = \mu$, and its value is determined by the condition that $\int n dV = N$. (In neutral systems μ is zero for the TF case, and is negative for the TFD case.) Thus, these two theories are special cases of our general theorem, and they cannot give rise to binding. Equation (3) for the TF case has already been obtained by Lee, Longmire, and Rosenbluth. If we introduce a correction for the electron correlation, the relation between Φ and n can be written in the form

$$(\Phi - \Phi_0)e - (5/3)\kappa_k n^{2/3} + \frac{4}{3}\kappa_i n^{1/3} + \frac{4}{3}\alpha_1 n^{1/3} / (n^{1/3} + \alpha_2) - \alpha_1 \frac{1}{3} n^{2/3} / (n^{1/3} + \alpha_2)^2 = 0 \quad (7)$$

with

$$\kappa_k = \frac{3}{10} (3\pi^2)^{2/3} e^2 a; \quad \kappa_i = \frac{3}{4} (3/\pi)^{1/3} e^2, \\ \alpha_1 = 0.056 e^2 / a, \quad \alpha_2 = 0.12 / a.$$

Inverting this relation we obtain n as a function of Φ . Thus, in this case too, binding is not possible.

We were unable to find a physical argument to show why the existence of the relation $n = f(\Phi)$ prohibits binding.

Since in reality stable molecules do exist, it would be interesting to see how far, and in what regions within an actual molecule the relation $n = f(\Phi)$ ceases to exist. This relation implies that the equipotential surfaces are also equipotential surfaces. Density maps computed for molecules do exist⁹; from them one is able to compute numerically the equipotential surfaces, and upon comparing the two sets of surfaces we may gain an idea as to where and how to improve the approximation leading to the density-potential relation.

FA Correction (Neutral Atoms)

Here $n = \sigma(\Phi_1 - \Phi_0)^{3/2}$, where $\Phi_1(x)$ is the potential seen by an atomic electron at the point x ; hence it is not equal to the total potential $\Phi(x)$ at x , observed by a small test charge, and which enters in (3) through $\mathbf{E} = -\text{grad}\Phi$. Conventionally, for a single atom, Φ_1 satisfies the differential equation $\Delta\Phi_1 = -4\pi\rho(M-1)/(M-4\pi\rho_A)$, if M electrons are present around the nucleus A . This correction, as is well known, leads to a finite radius for an atom.

The simplest generalization to a molecule with N electrons would be $\Delta\Phi_1 = -4\pi\rho(N-1)/N - 4\pi(\rho_A + \rho_B)$.

However, if the separation between A and B tends to infinity this equation is not solved by $\Phi_1^{(A)} + \Phi_1^{(B)}$, where $\Phi_1^{(A)}$ and $\Phi_1^{(B)}$ are the solutions for the isolated atoms A and B .

In fact, consider A and B very far apart and take a field point \mathbf{r} such that $|\mathbf{r}| \gg |\mathbf{r}_A - \mathbf{r}_B| \gg$ radius of A or B . Then $\Phi_1^{(A)} + \Phi_1^{(B)} = e/|\mathbf{r} - \mathbf{r}_A| + e/|\mathbf{r} - \mathbf{r}_B| \sim 2e/|\mathbf{r}|$, while $\Phi_1^{(A+B)} \sim e/|\mathbf{r}|$. The difficulty is that in Φ_1 we consider a field generated with 2 electrons removed, one from atom A and one from atom B . The problem is then to construct the proper FA correction for mole-

cules. This problem has not yet been satisfactorily solved.¹⁰ Somewhere else¹¹ we have pointed out that in the usual TF theory, as applied to atoms, the FA correction is uniquely determined by using a properly normalized closure relation which expresses the pair distribution function of the electrons through the singlet distribution function of the electrons. This is not the case for molecules since this closure condition can depend not only on N but on $|\mathbf{r}_A - \mathbf{r}_B|$ as well, and in such a way as to change the coefficient of ρ in the equation for Φ_1 from $(N-1)/N$ for small $|\mathbf{r}_A - \mathbf{r}_B|$ to $(\frac{1}{2}N-1)/(\frac{1}{2}N)$ for large separations. This leaves open the precise form of the FA correction for molecules; however, we are interested whether a binding force can arise for large separations. For this purpose it is sufficient to use the $(\frac{1}{2}N-1)/(\frac{1}{2}N)$ factor which gives

$$\Delta\Phi_1 = -4\pi\rho(\frac{1}{2}N-1)/(\frac{1}{2}N) - 4\pi(\rho_A + \rho_B). \quad (8)$$

To use our theorem we must find the relation between Φ_1 and Φ ; the latter obeys $\Delta\Phi = -4\pi\rho - 4\pi(\rho_A + \rho_B)$. If we denote the potential generated by the nuclei by Φ_{ex} , i.e. $\Delta\Phi_{\text{ex}} = -4\pi(\rho_A + \rho_B)$, the following relations exist,

$$\Phi_1 = \Phi(N-2)/N + (2/N)\Phi_{\text{ex}}; \\ \Phi = \Phi_1 N / (N-2) - 2\Phi_{\text{ex}} / (N-2); \quad (9)$$

or

$$\mathbf{E} = \mathbf{E}_1 N / (N-2) - 2\mathbf{E}_{\text{ex}} / (N-2),$$

with

$$\mathbf{E}_1 = -\text{grad}\Phi_1, \quad \mathbf{E}_{\text{ex}} = -\text{grad}\Phi_{\text{ex}}.$$

Outside the charge distribution $\Phi_1 = (2/N)\Phi_{\text{ex}}$, thus Φ vanishes outside the charge distribution, as it should be. (The $N=1$ case is excluded, since this results in a molecular ion.)

Substitute \mathbf{E} to compute \mathbf{F}_A . We find

$$\mathbf{F}_A = \int_S d\mathbf{S} \frac{E^2}{8\pi} \frac{N}{(N-2)} \int \rho \mathbf{E}_1 dV \\ + \frac{2}{(N-2)} \int \rho \mathbf{E}_{\text{ex}} dV. \quad (10)$$

The first term is positive, the second can be transformed into a surface integral over S the same way as before, and gives a positive contribution. The third term is $2(N-2)-1$ times the electric force acting on the electrons in the right half of the molecule due to ions A and B . Let $|\mathbf{r}_A - \mathbf{r}_B| = R$ be so large, that S does not go through the constituents A and B . Then E, ρ are zero on S and only the last term remains. This is the resultant of the electric force on the charge cloud around A due to nucleus B , $\mathbf{F}_A^{(B)}$, and due to nucleus A , $\mathbf{F}_A^{(A)}$. By symmetry \mathbf{F}_A must be along the line connecting A and B . Let us introduce the unit vector \mathbf{q} , pointing from B to A along this line. Thus $(\mathbf{q} \cdot \mathbf{F}_A)$ is negative if \mathbf{F}_A points to the left; thus the condition for binding is

⁹ P. R. Smith and J. W. Richardson, J. Phys. Chem. **69**, 3346 (1965).

¹⁰ Reference 1, p. 70.

¹¹ N. L. Balázs and R. A. Mould, Phys. Rev. **135**, A1560 (1964).

$(\mathbf{q} \cdot \mathbf{F}_A) < 0$. The first contribution is negative, $(\mathbf{q} \cdot \mathbf{F}_A^{(B)}) = -(Ne/2)^2(1/R^2)$. This term favors binding. The second contribution, $\mathbf{F}_A^{(A)}$ would vanish by symmetry if the charge cloud around A were spherical. In order to find $\mathbf{F}_A^{(A)}$ we need to solve Eq. (8). This we shall do in successive approximations. Assume

$$\begin{aligned}\Phi_1 &= \Phi_1^{(0)} + \Phi_1^{(1)} + \dots, & n &= n^{(0)} + n^{(1)} + \dots, \\ \Phi_0 &= \Phi_0^{(0)} + \Phi_0^{(1)} + \dots.\end{aligned}$$

We expect, and can later verify, that the iteration proceeds in inverse powers of R . The upper index denotes the order of smallness, the lower index labels the different functions Φ_0 , and Φ_1 . The iteration can be most easily described by Table I. Let the plane S subdivide the space into two half spaces, one containing B , the other A . The function will be given for the half spaces in which they appear in Table I. Thus, we first assume the TF solutions for isolated atoms, with the FA correction. This, however, is not quite right, because the tail of the solution for atom A , $e/|\mathbf{r}-\mathbf{r}_A|$, is present at atom B , and the tail of the solution for atom B , $e/|\mathbf{r}-\mathbf{r}_B|$ is present at atom A , while we have computed the density $n^{(0)}$ for each atom neglecting this tail. We correct this, computing an $n^{(1)}$ which is the second term in the Taylor-series expansion of n with respect to Φ_1 , and Φ_0 ; $n = \sigma(\Phi_1 - \Phi_0)^{3/2}$; Φ_0 is also expanded, and $\Phi_0^{(1)}$ is determined by the requirement that $\int n^{(1)} dV$ be zero. However, this $n^{(1)}$ now gives rise to an additional potential $\Phi_1^{(2)}$; this $\Phi_1^{(2)}$ in turn gives rise to a new correction $n^{(2)}$ in n ; etc.

We need only $n^{(1)}$ for our purposes, evaluated on atom A , i.e.

$$\begin{aligned}n^{(1)} &= \frac{3}{2}\sigma(\Phi_1^{(0)} - \Phi_0^{(0)})^{1/2}(\Phi_1^{(1)} - \Phi_0^{(1)}) \\ &= \frac{3}{2}\sigma^{2/3}[n^{(0)}]^{1/3}(e/|\mathbf{r}-\mathbf{r}_B| - \Phi_0^{(1)}).\end{aligned}$$

Let us put the origin of the coordinate system at nucleus A at a distance R from B , and expand $|\mathbf{r}-\mathbf{r}_B|^{-1}$. We get $n^{(1)}$ as

$$n^{(1)} = \frac{3}{2}\sigma^{2/3}e[n^{(0)}]^{1/3}[1/R - (\mathbf{r} \cdot \mathbf{q})/R^2 - \Phi_0^{(1)}/e],$$

where \mathbf{q} is a unit vector from nucleus B to A along R .

The integral of $n^{(1)}$ will vanish if we pick $\Phi_0^{(1)}/e = 1/R$, with

$$n^{(1)} = -\frac{3}{2}\sigma^{2/3}e[n^{(0)}]^{1/3}(\mathbf{r} \cdot \mathbf{q})/R^2.$$

Since $-(\mathbf{r} \cdot \mathbf{q})$ is positive to the left of A , we see that the center of the charge cloud around A moved towards B . The force along \mathbf{q} due to nucleus A is

$$\begin{aligned}-\int \frac{1}{2}Ne en^{(1)}[(\mathbf{q} \cdot \mathbf{r})/r^3]dV \\ = \frac{1}{2}Ne^2(1/R^2)\left(\frac{3}{2}\right)\sigma^{2/3}e \int [n^{(0)}]^{1/3}(\mathbf{r} \cdot \mathbf{q})^2/r^3 dV \\ = \frac{1}{2}Ne^2(1/R^2)\{2\pi\sigma^{2/3}e \int [n^{(0)}]^{1/3}r dr.\end{aligned}$$

TABLE I. Approximation scheme to Thomas-Fermi equations with the Amaldi correction for the widely separated atoms A and B .

| B half space | S | A half space |
|--|--|--|
| Zeroth order | | |
| $\Phi_1^{(0)} = \Phi_1$ $\Phi_0^{(0)} = \Phi_0$ $n^{(0)} = n$ | TF solution for isolated B atom | $\Phi_1^{(0)} = \Phi_1$ $\Phi_0^{(0)} = \Phi_0$ $n^{(0)} = n$ |
| First order | | |
| $\Phi_1^{(1)} = e/ \mathbf{r}-\mathbf{r}_A $ $n^{(1)} = \frac{3}{2}\sigma(\Phi_1^{(0)} - \Phi_0^{(0)})^{1/2}$ $(\Phi_1^{(1)} - \Phi_0^{(1)})$ $\Phi_0^{(1)}$ determined by $\int n^{(1)} dV = 0$ | | $\Phi_1^{(1)} = e/ \mathbf{r}-\mathbf{r}_B $ $n^{(1)} = \frac{3}{2}\sigma(\Phi_1^{(0)} - \Phi_0^{(0)})^{1/2}$ $(\Phi_1^{(1)} - \Phi_0^{(1)})$ $\Phi_0^{(1)}$ determined by $\int n^{(1)} dV = 0$ |
| Second order | | |
| | $\Phi_1^{(2)} = \int dV' n(\mathbf{r}')/ \mathbf{r}-\mathbf{r}' $ $n^{(2)} = \frac{3}{2}\sigma(\Phi_1^{(0)} - \Phi_0^{(0)})^{1/2}(\Phi_1^{(2)} - \Phi_0^{(2)})$ $+ \frac{3}{2}\sigma(\Phi_1^{(0)} - \Phi_0^{(0)})^{-1/2}(\Phi_1^{(1)} - \Phi_0^{(1)})^2$ etc. | |

Introduce the standard variables $x = r/\mu^*$,

$$n^{(0)} = \left[\frac{1}{2}N/4\pi\mu^{*3}\right]\left[\frac{1}{2}N/(\frac{1}{2}N-1)\right](\varphi/x)^{3/2},$$

where φ is the solution of the dimensionless TF equation $\varphi'' = \varphi^{3/2}/x^{1/2}$, with the boundary condition $x_0\varphi'(x_0) = -2/N$, and

$$\mu^* = (4\pi\sigma)^{-2/3}e^{-1}(\frac{1}{2}N)^{-1/3}\left[\frac{1}{2}N/(\frac{1}{2}N-1)\right]^{2/3};$$

$r_0 = \mu^*x_0$ is the radius of the isolated atom. (This μ^* should not be confused with μ , the chemical potential.) This gives

$$(\mathbf{q} \cdot \mathbf{F}_A^{(A)}) = \left[\frac{1}{2}Ne^2/R^2\right]\left\{\frac{1}{2}\left[\frac{\frac{1}{2}N}{(\frac{1}{2}N-1)}\right]\int_0^{x_0} dx(x\varphi)^{1/2}\right\}.$$

$(\mathbf{q} \cdot \mathbf{F}_A^{(B)})$ is $-\frac{1}{2}Ne^2/R^2$; hence the existence of binding will be determined by the condition

$$\frac{1}{2}\left[\frac{\frac{1}{2}N}{(\frac{1}{2}N-1)}\right]\int_0^{x_0} dx(x\varphi)^{1/2} < 1.$$

The latter integral must be evaluated approximately, and will depend on N . A crude numerical integration gives for the integral the value 5.7 for $\frac{1}{2}N = 10$; 4.7 for $\frac{1}{2}N = 5$; 1.1 for $\frac{1}{2}N = 2$. Thus, no binding will arise for even such a low value of $\frac{1}{2}N$ as 2.

Weizsäcker Correction

Put $n = \chi^2$; then, according to Weizsäcker, the relation between the potential Φ and χ is given by

$$\begin{aligned}(e\Phi + \mu)\chi &= (5/3)\kappa_k\chi^{7/3} - 4\kappa_i\Delta\chi, \\ \kappa_k &= (3e/5)\sigma^{-2/3}, \\ \kappa_i &= e^2a/8, \text{ or } e^2a/32.\end{aligned}\quad (11)$$

The first term on the right gives the TF theory, the second is the Weizsäcker correction. (The factor $\frac{1}{8}$ is given by Weizsäcker; the more accurate factor $\frac{1}{32}$ was

obtained by Kompaneets and Pavlovskii, and by Baraff and Borowitz.¹² Since μ is constant, we can immediately insert $(e\Phi + \mu)$ in \mathbf{F} , in place of $e\Phi$. The first term gives

$$\begin{aligned}
 F_\alpha &= -e \int_{V_A} dV n E_\alpha = \int_{V_A} dV n \partial(e\Phi) / \partial x_\alpha = \int_{V_A} dV \chi^2 \partial[(5/3)\kappa_k \chi^{4/3} - 4\kappa_i \Delta \chi / \chi] / \partial x_\alpha \\
 &= \int_{V_A} dV \{ (5/3)\kappa_k (\frac{4}{3}) \chi^{7/3} \partial \chi / \partial x_\alpha - 4\kappa_i (\chi \partial^3 \chi / \partial^2 x_\beta \partial x_\alpha - \partial \chi / \partial x_\alpha \partial^2 \chi / \partial^2 x_\beta) \} \\
 &= \int_{V_A} dV \{ \partial[\frac{2}{3}\kappa_k \chi^{10/3} \delta_{\alpha\beta}] / \partial x_\beta - \partial 4\kappa_i (\chi \partial^2 \chi / \partial x_\alpha \partial x_\beta - \partial \chi / \partial x_\alpha \partial \chi / \partial x_\beta) / \partial x_\beta \} \\
 &= \int_S dS_\beta [\frac{2}{3}\kappa_k \chi^{10/3} \delta_{\alpha\beta} + 4\kappa_i (\partial \chi / \partial x_\alpha \partial \chi / \partial x_\beta - \chi \partial^2 \chi / \partial x_\alpha \partial x_\beta)] \\
 &= - \int_S (dS_i)_\beta [\text{same integrand}] = - \int_S (dS_i)_\beta \{ \frac{2}{3}\kappa_k n^{5/3} \delta_{\alpha\beta} + (2\kappa_i / n) [(\partial n / \partial x_\alpha)(\partial n / \partial x_\beta) - n(\partial^2 n / \partial x_\alpha \partial x_\beta)] \}. \quad (12)
 \end{aligned}$$

Let us take the direction from B to A the positive x direction. Then, in the integral over S only the first and last terms survive, (the second vanishes by symmetry); and we obtain for $(F_A)_x$

$$(F_A)_x = \int (dS_i)_x \{ E^2 / 8\pi + \frac{2}{3}\kappa_k n^{5/3} - 2\kappa_i (\partial^2 n / \partial x^2) \}. \quad (13)$$

For binding to be possible $\partial^2 n / \partial x^2$ must be positive on S , and large enough to balance the other terms.

Consider now the nuclei so far apart that we can approximate χ midway between them by the sum of the asymptotic solutions obtained for the individual atoms, $\chi_A(s_A)$, $\chi_B(s_B)$; where s_A is the distance from nucleus A , and s_B is the distance from nucleus B . They obey asymptotically the differential equations

$$\Delta \chi_A + (\mu / 4\kappa_i) \chi_A = 0, \quad \Delta \chi_B + (\mu / 4\kappa_i) \chi_B = 0,$$

which are indeed obtained from (11) if we neglect powers of χ and neglect $e\Phi$ compared to μ ; the first we can do, since n and χ tend to zero in the central region as the separation tends to infinity; the second is trivially permitted since, as the separation increases Φ tends to zero in this region while the constant μ tends to $\mu_A = \mu_B$, the chemical potential of the isolated atom. (The integrability of n requires that this μ be negative.) The solution will then be of the form $\chi = C(e^{-s_A/l} / s_A + e^{-s_B/l} / s_B)$, where C is a constant and l is the decay length $l = (4\kappa_i / |\mu|)^{1/2}$, $\mu < 0$.

We estimate now the three terms in the integrand of Eq. (13). Let n be the density midway between the two nuclei, which are at a large distance $2R$ from each other. Around the midpoint the electric field due to the charge

¹² A. S. Kompaneets and E. S. Pavlovskii, Zh. Eksperim. i Teor. Fiz. **31**, 427 (1956) [English transl.: Soviet Phys.—JETP **4**, 328 (1957)]; G. A. Baraff and S. Borowitz, Phys. Rev. **121**, 1704 (1961); see also N. L. Balázs, *ibid.* **134**, A841 (1964).

the TF result; the second term can be integrated by parts; we finally obtain for the α component of \mathbf{F} , ($\alpha=1, 2, 3$; summation convention)

clouds around A and B can be uniquely expanded in inverse powers of R . The leading term is the same as the Coulomb force due to two point charges; one, carrying the unshielded charge around A located at nucleus A , the other carrying the unshielded charge around B located at nucleus B . Since the amount of unshielded charge present around each nucleus is about $4\pi R^2 l n e$, this gives an electric field of order $2(4\pi R^2 l n e) / R^2$. Then, the three terms in the integrand are of the following orders:

$$8\pi(l e)^2 n^2, \quad (\frac{2}{3})\kappa_k n^{5/3}, \quad -2\kappa_i n / l^2.$$

As we let R tend to infinity n tends to zero. The first term is of order n^2 , the second of order $n^{5/3}$, while the last one of order n . Thus the last term will predominate and hence an attractive force will arise between the widely separated constituents; this force goes to zero exponentially as the separation tends to infinity. The Weizsäcker correction stabilized the molecule.

Suppose now that we wish to include the Dirac and Gombás correction terms as well. Will the Weizsäcker term lead again to stabilization? The answer is yes. Now Eq. (11) will be amended by terms which are proportional to $n^{1/3}$ and $n^{2/3}$ for small n . Hence, around the midpoint the asymptotic form of this equation for large separation remains the same and we can estimate in \mathbf{F}_A each term as before. The new terms in the equation replacing (11) give rise to new terms in the integrand of \mathbf{F}_A which are proportional to $n \times n^{1/3}$ and $n \times n^{2/3}$; hence, for small n they are again negligible compared to the stabilizing term, which is proportional to n . Thus a stable molecule will arise again. Indeed, an approximate numerical calculation by Gombás¹³ shows that within the Thomas-Fermi-Dirac-Weizsäcker (TFDW) theory an N_2 molecule is stable, while

¹³ P. Gombás, Acta Phys. Acad. Sci. Hung. **9**, 461 (1959). This paper uses the $\frac{1}{3}$ factor in the Weizsäcker correction.

Sheldon² obtains no stable N_2 molecule omitting the Weizsäcker term.

IV. GENERALIZATIONS

Our results should be generalized in different directions; first, to homonuclear diatomic molecular ions; second, to general molecules, finally to general molecular ions. As far as diatomic molecular ions are concerned, the situation is as follows. In Eq. (2) there is no additional contribution to \mathbf{F} coming from the integration over S' , since the field falls off as $1/r^2$, and the surface integral contains as the integrand the square of the field. Hence all our results in the TF, TFD, and (TF+correlation correction) cases are unchanged. We have seen that the FA correction does not generate binding for most cases of interest. This situation will be even worse if the molecule is not neutral. For the TF theory with the Weizsäcker correction as applied to ions further work is needed, since an additional term, independent of n appears in Eq. (2), which upsets the method used before.

Let us generalize now our results to a general polynuclear molecule. First, take the case where $n=f(\Phi)$; this gave no binding for homonuclear diatomic molecules. Observe that the crucial requirement in the proof was the existence of surfaces S' and S . The surface S' surrounds the molecule, and on it the electric field is zero. As long as $\int ndV$ converges, such a surface will exist. S had the property that it separated one nucleus from the rest and had no electric field across it, i.e., it was orthogonal to all equipotential surfaces it intersected. Will S always exist? If the surface is given by $g(x,y,z)=C$, g satisfies the partial differential equation $\text{grad}g \cdot \text{grad}\Phi=0$. The existence of this surface was assured in the homonuclear diatomic case by symmetry. For the general case, we proceed in two steps. First we show the existence of this surface for a special arrangement of the nuclei, then we show that by changing this arrangement we can only deform the surface but cannot destroy its existence. Once we have shown this, the proof of the impossibility of binding goes through exactly as before. Consider, then a collection of nuclei and electrons, and arrange all nuclei except for one in a small spherical bunch B fixing them, say, on the surface of a small sphere. Further away, fix nucleus A . Surround this configuration with the electrons according to the law $n=f(\Phi)$, where Φ is the solution of Poisson's equation. Except for the immediate vicinity of B , this arrangement will have a cylindrical symmetry around the line connecting B with A . (In the immediate

vicinity of B the fact that B is not quite spherical will disturb slightly this symmetry.) Now consider a plane through B and A , and carry in this plane, along a given path, a small positive test charge from B to A . In the immediate vicinity of each end the electric field along the path will be repulsive, thus the projection of E onto the path will have opposite signs. Since the electric field is continuous, there must be at least one point along the path where this projection is zero. Mark these points. Repeat this for many paths. The same remark applies to each. Now pick on each path that point which is nearest to A . Connect these. You get a curve C . Rotate the plane containing this curve around the connecting line AB . The curve C will generate the surface S . We have constructed the required solution of $\text{grad}g \cdot \text{grad}\Phi=0$ for this special configuration. But the solution of this partial differential equation depends continuously on the coefficients, which in turn depend continuously on the location of the nuclei. (To avoid any difficulties we shall consider the positive nuclei as small charged spheres, and we admit only such configurational changes which do not require the fusion, or splitting of the positive nuclei. Since in the construction their number is left arbitrary, this is no restriction.) Hence, by changing the configuration of the nuclei we will change the location and shape of surface S , but it always remains in existence. Knowing that an S exists, we can immediately show, as before, that no theory which gives the electron density as a function of potential alone, can describe a stable molecule.

For the theory amended by the FA correction and Weizsäcker correction the generalization is more difficult, and we intend to return to it later. The FA correction must be treated differently, since the proof did not depend only on the existence of the surface S . For the Weizsäcker correction a difficulty arises, since we used the fact that S is a symmetry plane, twice: first, to show that on S the vector \mathbf{E} has no normal component; second, that on it $\text{grad}n$ has no normal component either. The first step can be generalized; however, in general, the second does not follow from the first and our proof breaks down.

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