

Upper- and Lower-Bound Energy Calculations for Atoms and Molecules in the Thomas-Fermi Theory*

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Using simple functions, upper and lower bounds for the Thomas-Fermi energies of atoms and homonuclear diatomic molecules at various internuclear separations are calculated which differ by less than 0.2% in the atomic case and at most by 0.5% for molecules. The calculation verifies that for this model molecules are not stable for short and intermediate nuclear separations. The possibility of a long-range attraction is also examined, and again the conclusions are found to be in agreement with Teller's theorem.

I. INTRODUCTION

IN the framework of the Thomas-Fermi (TF) model,¹⁻³ the electron cloud in the atomic or molecular system is treated as though it were a completely degenerate electron gas obeying Fermi-Dirac statistics. Application of the statistical theory to a neutral system leads to

$$\rho = \lambda^{-3/2} V^{3/2}, \quad (1)$$

where ρ is the electron density, V is the electric potential, and $\lambda = \frac{1}{2}(3\pi^2)^{2/3} ea_0$. Atomic units will be used throughout. With the application of Poisson's equation and Eq. (1), the TF differential equation is obtained:

$$\nabla^2 V = -4\pi \sum_i Z_i \delta(\mathbf{r} - \mathbf{r}_i) + 4\pi \lambda^{-3/2} V^{3/2}, \quad (2)$$

where Z_i is the charge of the i th nucleus and \mathbf{r}_i is its position vector. Again the statistical theory can be invoked to arrive at an expression for the total energy:

$$E = \frac{3}{5}\lambda \int \rho^{5/3} dv - \int V_N \rho dv - \frac{1}{2} \int V_e \rho dv + U_N, \quad (3)$$

where

$$V_N = \sum_i \frac{Z_i}{r_i},$$

$$V_e = - \int \frac{\rho(\mathbf{r}') dv'}{|\mathbf{r} - \mathbf{r}'|},$$

$$V = V_e + V_N,$$

and

$$U_N = \sum_{j>i} \frac{Z_j Z_i}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Furthermore it can be shown that the functional \bar{E} , derived from E by replacing ρ with any normalized

trial density function $\bar{\rho}$, leads to an upper bound for the exact TF energy.⁴

Firsov⁵ has demonstrated the existence of another functional \bar{H} which provides a lower bound to the TF energy.

$$\bar{H} = \frac{1}{8\pi} \int \bar{f} \nabla^2 \bar{f} dv - \frac{2}{5} \lambda^{-3/2} \int (V_N - \bar{f})^{5/2} dv + U_N. \quad (4)$$

The following restrictions hold for the trial function \bar{f} : (a) $\bar{f} < V_N$ in order that the second integral be real (if $\bar{f} = V_N$ then $H = -\infty$); (b) \bar{f} must vanish at infinity. Also, the positive root is always taken in the second integration in (4). For the exact solution f (that \bar{f} which completely maximizes \bar{H}), one has the relation

$$f = -V_e(\rho). \quad (5)$$

In the calculation which follows we will use an analogous relation to generate \bar{f} , namely,

$$\bar{f} = -V_e(\bar{\rho}). \quad (5')$$

Thus, two functionals, (3) and (4), are available which are capable of yielding an upper and lower bound, respectively, to the TF energy of an atomic or molecular system.

In the atomic and in the molecular calculation, the nuclear charge has been set equal to unity. This is not a limitation since a scaling theorem exists in both the atomic and molecular case.⁶ For an atom,

$$E(Z) = Z^{7/3} E(1). \quad (6)$$

For a homonuclear diatomic molecule,

$$E(R, Z) = Z^{7/3} E(RZ^{1/3}, 1), \quad (7)$$

where R is the internuclear separation. Equation (7) follows directly from consideration of Eq. (3) for a homonuclear diatomic molecule.

II. ATOMS

The minimization procedure has been applied to the atomic problem with good results by Jensen.⁷ The trial

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¹ L. H. Thomas, Proc. Cambridge Phil. Soc. 23, 542 (1927).

² E. Fermi, Z. Physik 48, 73 (1928).

³ P. Gombas, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949).

⁴ Reference 3, p. 31.

⁵ O. B. Firsov, Zh. Eksperim. i Teor. Fiz. 32, 1464 (1957) [English transl.: Soviet Phys.—JETP 5, 1192 (1957)].

⁶ Reference 3, p. 60.

⁷ H. Jensen, Z. Physik 77, 722 (1932).

density used for the calculation was

$$\tilde{\rho} = \frac{Z}{A} \frac{e^{-x}}{x^3} [P(x)]^3, \quad (8)$$

where A is a normalization factor chosen so that $\int \tilde{\rho} dv = Z$, $x = (\alpha Z^{1/3} r)^{1/2}$, α is a variational parameter, and $P(x) = 1 + Cx$, where C is another variational parameter. Using this density and the upper-bound functional (3), Jensen obtained the results displayed in Table I. A poor result was obtained for $P(x) = 1$.

We have obtained a lower bound to the energy from Eqs. (4) and (5') using as an approximate density

$$\tilde{\rho} = \frac{Z}{A} \frac{e^{-x}}{x^3}, \quad (9)$$

corresponding to $P(x) = 1$ in the Jensen approximation. Equation (5') then yields⁸

$$\tilde{f} = \int \frac{\tilde{\rho}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} dv' = \alpha Z^{4/3} \left[\frac{1 - e^{-x}(x+1)}{x^2} \right]. \quad (10)$$

Substituting (10) into (4), an expression for the lower-bound energy is obtained. The first integral in (4), $\int \tilde{f} \nabla^2 \tilde{f} dv$, can be done analytically, whereas the second integration $\int (V_N - \tilde{f})^{5/2} dv$ must be done numerically.⁹ With this simple choice for \tilde{f} , a surprisingly good result is obtained after optimization with respect to the variational parameter α . In fact, a smaller deviation from the exact value is obtained than with the more complicated function used in the upper-bound calculation. These lower-bound results are shown in Table I, along with the upper-bound values and the exact TF energies.

In Table II we have tabulated an approximate TF function $\tilde{\varphi}$. This is defined as follows. Since $V = V_e + V_N$ we have from (5) the exact solution

$$V = V_N - f. \quad (11)$$

This then suggests defining an approximate \tilde{V} according to (10) and (11). From this \tilde{V} we calculate an approximate dimensionless TF function defined as

$$\tilde{\varphi} = (r/Z) \tilde{V}. \quad (12)$$

TABLE I. Calculations for atoms.

Method	Energy ($Z=1$) (a. u.)	α	C
Jensen (upper bound)	-0.76776	10.9107	0.265
Exact	-0.76873
This work (lower bound)	-0.76920	4.1024	...

⁸ The integration is the same as that used to determine the electrostatic potential produced by a spherically symmetric charge distribution.

⁹ All computations for this work were performed on the CDC-1604 computer.

TABLE II. Dimensionless TF function.

t	$\tilde{\varphi}$ (this work)	φ^a	$\tilde{\varphi}^b$
0	1.000	1.000	...
0.05	0.932	0.935	0.97
0.10	0.877	0.882	0.89
0.20	0.790	0.793	0.79
0.30	0.720	0.721	0.71
0.50	0.612	0.607	0.59
1.00	0.433	0.425	0.42
4.00	0.107	0.108	0.109
5.00	0.0743	0.0788	0.0783
10.00	0.0170	0.0244	0.0207
20.00	0.00186	0.0058	0.0027

^a Reference 11.

^b Reference 12.

The exact φ satisfies the dimensionless TF equation¹⁰

$$\varphi'' = \varphi^{3/2} / t^{1/2}, \quad (13)$$

where $t = r/\mu$, $\mu = 0.8853a_0/Z^{1/3}$, and $\varphi = (r/Z)V$. Then, using (10), (11), and (12),

$$\tilde{\varphi} = e^{-x}(x+1) = e^{-1.905t^{1/2}}(1.905t^{1/2}+1). \quad (14)$$

This approximate $\tilde{\varphi}$ is compared with the numerical solution of Bush and Caldwell¹¹ and also with Brinkman's¹² approximation. Equation (14) shows reasonably good agreement for such a simple function, although it displays incorrect behavior as $t \rightarrow \infty$.

III. HOMONUCLEAR DIATOMIC MOLECULES

A. Intermediate Internuclear Separations

Teller¹³ and more recently Balázs¹⁴ have shown that the TF model can not lead to molecular binding. Firsov¹⁵ has performed a calculation utilizing the upper- and lower-bound technique; however, it was not done accurately enough to clearly point out that binding was not possible. Townsend and Handler¹⁶ have solved the TF equation numerically for the homonuclear diatomic molecule. Their results for the intermolecular potential indicate that binding will not occur for intermediate separations. One of the objectives of the present calculation is to confirm, with the help of Firsov's lower-bound method, that binding does not occur. At the same time it provides a simple analytical form for the molecular electron density.

We have approximated the molecular density by a superposition of the approximate atomic functions (8) centered on nucleus A and B :

$$\tilde{\rho}_{\text{mol}} = \tilde{\rho}_A + \tilde{\rho}_B. \quad (15)$$

The parameter C in (8) is not varied but set equal to

¹⁰ Reference 3, p. 40.

¹¹ V. Bush and S. H. Caldwell, Phys. Rev. **38**, 1898 (1931).

¹² H. C. Brinkman, Physica **20**, 44 (1954).

¹³ E. Teller, Rev. Mod. Phys. **34**, 627 (1962).

¹⁴ N. L. Balázs, Phys. Rev. **156**, 42 (1967).

¹⁵ O. B. Firsov, Zh. Eksperim. i Teor. Fiz. **33**, 696 (1958) [English transl.: Soviet Phys.—JETP **6**, 534 (1958)].

¹⁶ J. R. Townsend and G. S. Handler, J. Chem. Phys. **36**, 3325 (1962).

TABLE III. Upper-bound molecular energies for $Z=1$ (hydrogen molecule) in atomic units.

R^a	α	$\tilde{E}-U_N$	$\tilde{E}-2E_{\text{TF atom}}$
0	13.75	-3.8693	∞
0.0780	12.80	-3.2430	11.1250
0.3296	12.14	-2.7160	1.8557
0.7789	11.55	-2.3412	0.4801
1.4278	11.21	-2.0911	0.1467
2.2647	11.04	-1.9290	0.0500
3.2829	10.97	-1.8231	0.0189
4.8091	10.94	-1.7524	0.0082
5.8597	10.92	-1.7038	0.0044
7.4190	10.92	-1.6707	0.0026
9.1610	10.92	-1.6443	0.0023
∞	10.91	-1.5355	0.0019

^a The energies were calculated for regularly spaced values of the reduced quantity $(\alpha R)^{1/2}$.

the optimal atomic value. $\tilde{\rho}_{\text{mol}}$ was substituted into (3) and the integrations were performed numerically. The results are given in Table III along with the optimized values of the variational parameter α . The electronic energy $\tilde{E}-U_N$, as well as the potential-energy curve (with respect to the exact separated TF atoms) are given.

Similarly in the lower-bound calculations a superposition of the functions used in the atomic calculation was used:

$$\tilde{f}_{\text{mol}} = \tilde{f}_A + \tilde{f}_B. \quad (16)$$

The results of the lower-bound calculations are listed in Table IV.

The results for the upper- and lower-bound calculations differ at most by about 0.5% in the electronic energy. It is particularly useful to study the lower-bound values for the TF molecule since these can determine with certainty if the molecule will be unbound in the region considered. As long as $\tilde{H}-2E_{\text{TF atom}} > 0$ the molecule cannot bind. This is the case up to the separation $R=7a_0$ for $Z=1$. The results can be extended to larger separations since the approximate lower bound for the molecular energy \tilde{H} has been referred to an exact separated atom system whose energy is -1.5375 . However, the separated atom energy for \tilde{f} is -1.5384 . Thus the lower-bound potential curve can be expected to be lower than the exact curve by about 0.0009, which is the difference in the approximate and the exact separated atom energies, as R becomes larger.

TABLE IV. Lower-bound molecular energies for $Z=1$ (hydrogen molecule) in atomic units.

R	α	$\tilde{H}-U_N$	$\tilde{H}-2E_{\text{TF atom}}$
0	5.169	-3.8765	∞
0.1960	5.120	-2.9490	3.6905
0.8254	4.846	-2.3290	0.4200
1.9952	4.511	-1.9757	0.0629
3.7434	4.274	-1.7946	0.0100
6.0061	4.162	-1.7026	0.0013
8.7362	4.121	-1.6523	-0.0004
11.9296	4.107	-1.6221	-0.0008
∞	4.102	-1.5384	-0.0009

This is sufficient to extend the instability range out to the largest R tabulated, which is close to $12a_0$ for $Z=1$. For a molecule such as N_2 ($Z=7$) it can be shown with Eq. (7) that binding should not occur in the TF sense up to at least $6a_0$.

B. Large Internuclear Separations

As pointed out, one has at his disposal both an upper-bound and a lower-bound functional for the TF system. In the following section these expressions are used to develop upper and lower bounds for the energy of a diatomic molecule at very large separations and hence provide verification of Teller's theorem at long ranges. For extended separations, the leading term in an R^{-1} expansion should be repulsive rather than attractive, as is the case for real molecules (Van der Waals attraction).

If a linear combination of exact TF atomic functions¹⁷ is used in (3) and (4), the following bounded expressions for the total energy are obtained¹⁵ (where $Z=1$):

$$E(R) = \lambda \int \left[\frac{3}{5}(\rho_{0A} + \rho_{0B})^{2/3} - \frac{1}{2}(\rho_{0A}^{2/3} + \rho_{0B}^{2/3}) \right] \times (\rho_{0A} + \rho_{0B}) dv - \frac{1}{2} \int \left(\frac{1}{r_A} + \frac{1}{r_B} \right) (\rho_{0A} + \rho_{0B}) dv + \frac{1}{R} \quad (17)$$

and

$$H(R) = \lambda \int \left[\frac{1}{2}(\rho_{0A} + \rho_{0B}) - \frac{2}{5}(\rho_{0A}^{2/3} + \rho_{0B}^{2/3})^{3/2} \right] \times (\rho_{0A}^{2/3} + \rho_{0B}^{2/3}) dv - \frac{1}{2} \int \left(\frac{1}{r_A} + \frac{1}{r_B} \right) (\rho_{0A} + \rho_{0B}) dv + \frac{1}{R}. \quad (18)$$

For the TF atom one has the expression

$$E_{\text{TF atom}} = \frac{\lambda}{10} \int \rho_0^{5/3} dv - \frac{1}{2} \int \frac{\rho_0}{r} dv. \quad (19)$$

With Eqs. (17)–(19), one obtains the potential-energy curves relative to two TF atoms for the upper bound;

$$E_U(R) = E(R) - 2E_{\text{TF atom}} = \frac{3}{5}\lambda \int [(\rho_{0A} + \rho_{0B})^{5/3} - \rho_{0A}^{5/3} - \rho_{0B}^{5/3}] dv - \frac{1}{2}\lambda \int (\rho_{0A}^{2/3}\rho_{0B} + \rho_{0B}^{2/3}\rho_{0A}) dv - \frac{1}{2} \int \left(\frac{\rho_{0A}}{r_B} + \frac{\rho_{0B}}{r_A} \right) dv + \frac{1}{R}, \quad (20)$$

¹⁷ ρ_{0A} and ρ_{0B} refer to the exact TF atomic densities placed on nucleus A and B , respectively.

and for the lower bound,

$$\begin{aligned}
 H_L(R) &= H(R) - 2E_{\text{TF atom}} \\
 &= \frac{2}{3}\lambda \int [\rho_{0A}^{5/3} + \rho_{0B}^{5/3} - (\rho_{0A}^{2/3} + \rho_{0B}^{2/3})^{5/2}] dv \\
 &\quad + \frac{1}{2}\lambda \int (\rho_{0A}^{2/3}\rho_{0B} + \rho_{0B}^{2/3}\rho_{0A}) dv \\
 &\quad - \frac{1}{2} \int \left(\frac{\rho_{0A}}{r_B} + \frac{\rho_{0B}}{r_A} \right) dv + \frac{1}{R}. \quad (21)
 \end{aligned}$$

Since (20) and (21) are symmetric about the reflection plane of the nuclei we need only consider the half-space containing nucleus A when examining the behavior of the integrals for large R . Then $\int dv'$ will denote an integration over the half-space containing nucleus A and $\int dv$ is the integration over the entire space. In this half-space $\rho_{0A} > \rho_{0B}$. This allows us to expand certain expressions in (20) and (21) using a Taylor series:

$$(\rho_{0A} + \rho_{0B})^{5/3} = \rho_{0A}^{5/3} \left[1 + \frac{5}{3} \frac{\rho_{0B}}{\rho_{0A}} + \frac{5}{9} \left(\frac{\rho_{0B}}{\rho_{0A}} \right)^2 + \dots \right] \quad (22)$$

and

$$\begin{aligned}
 (\rho_{0A}^{2/3} + \rho_{0B}^{2/3})^{5/2} &= \rho_{0A}^{5/3} \left[1 + \frac{5}{2} \left(\frac{\rho_{0B}}{\rho_{0A}} \right)^{2/3} \right. \\
 &\quad \left. + \frac{15}{8} \left(\frac{\rho_{0B}}{\rho_{0A}} \right)^{4/3} + \dots \right]. \quad (23)
 \end{aligned}$$

Upon substitution of (22) and (23) into (20) and (21) and using

$$\int \frac{\rho_{0A}}{r_B} dv = \int \frac{\rho_{0B}}{r_A} dv,$$

we have

$$\begin{aligned}
 E_U(R) &= \lambda \int [\rho_{0B}\rho_{0A}^{2/3} - \rho_{0A}\rho_{0B}^{2/3}] dv' - \int \frac{\rho_{0A}}{r_B} dv + \frac{1}{R} \\
 &\quad + \int \left[-\frac{6}{5} \lambda \rho_{0B}^{5/3} + \frac{2}{3} \lambda \rho_{0B}^2 \rho_{0A}^{-1/3} + \dots \right] dv' \quad (24)
 \end{aligned}$$

and

$$\begin{aligned}
 H_L(R) &= \lambda \int [\rho_{0B}\rho_{0A}^{2/3} - \rho_{0A}\rho_{0B}^{2/3}] dv' - \int \frac{\rho_{0A}}{r_B} + \frac{1}{R} \\
 &\quad + \int \left[\frac{2}{3} \lambda \rho_{0B}^{5/3} - \frac{2}{3} \lambda \rho_{0B}^{4/3} \rho_{0A}^{1/3} + \dots \right] dv'. \quad (25)
 \end{aligned}$$

For very large R , the higher-order terms in the last integration in (24) and (25) can be shown to vanish at least as fast as R^{-7} by using the fact that

$$\lim_{r \rightarrow \infty} \rho_0 = \left(\frac{3\lambda}{\pi} \right)^3 \frac{1}{r^6}. \quad (26)$$

Hence for very large R , $E_U(R) - H_L(R) \sim R^{-7}$, so any term of lower order than R^{-7} in either (24) or (25) is exact for large separations. Thus up to order R^{-6} one can write the TF interaction potential as

$$\begin{aligned}
 E_{\text{mol}}(R) &= \lambda \int [\rho_{0B}\rho_{0A}^{2/3} - \rho_{0A}\rho_{0B}^{2/3}] dv' \\
 &\quad - \int \frac{\rho_{0A}}{r_B} dv + \frac{1}{R}. \quad (27)
 \end{aligned}$$

With some analysis and the use of (26), one can show that

$$E_{\text{mol}}(R) = CR^{-6}, \quad (28)$$

where

$$C = \left(\frac{3}{\pi} \right)^3 \lambda^4 \int \rho_{0A}^{2/3} dv.$$

Since $C > 0$ the leading term in the expansion for large R leads to repulsion.

IV. CONCLUSION

The results of this investigation are in complete agreement with Teller's theorem. At normal separations this was demonstrated by a calculation, while at very large separations the leading term in the R^{-1} expansion was shown to be repulsive. At the same time this calculation also provides a simple approximate expression for the electron density of homonuclear diatomic molecules in the TF framework.

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