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Interaction Energy of Atoms For Small Nuclear Separations

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As is well known, the Thomas-Fermi equation for electrons can be obtained by minimizing a certain functional of the spatial density distribution. At the same time a functional of a certain function of the coordinates is established, such that its maximum value gives the same electron energy. It is shown for two nuclei that if one inserts into these functionals the sum of the electron densities and the sum of f functions which cause the single-nucleus functionals to be, respectively, minimum and maximum, then the relative difference between these functionals will not exceed 5%. The electron energies then lie between the two values of these functionals.

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1. MINIMIZATION PRINCIPLE

FOR SEPARATIONS less than the dimensions of a Bohr orbit $\sim 10^{-8}$ cm between the nuclei of interacting atoms, the interaction between the external parts of the electron shells of the atoms contributes a term to the atomic interaction energy which is small compared with the energy change of the internal parts of the electron shells of the system. Thomas-Fermi methods are applicable to the internal parts of the electron shells.

Because of the relation between the electron density ρ and the kinetic energy of the electrons, the total electron energy of the system of interacting atoms is given by (see, for instance, Gombas[1])

$$e^{-2}H = \frac{3}{5}\lambda\int\rho^{5/3}\,dv - \int\sum_i\frac{Z_i}{r_i}\rho\,dv + \iint\frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')\,dv\,dv'}{|\mathbf{r}-\mathbf{r}'|}, \tag{1}$$

where $\lambda = (3\pi^2)^{2/3}h^2/2me^2 \approx 2.5\times10^{-8}$ cm, and Z_ie are the nuclear charges. We shall henceforth take the electron charge e equal to unity; r_i is the distance to the ith nucleus. The first term on the right of Eq. (1) is the kinetic energy of the electrons according to the Thomas-Fermi model, the second is the interaction energy of the electrons with the nuclei, and the third is the interaction energy among the electrons.

The density ρ is found by minimizing H. Variation of H with respect to ρ gives

$$\lambda\rho_0^{2/3} = \sum\frac{Z_i}{r_i} - \int\frac{\rho_0(\mathbf{r}')\,dv}{|\mathbf{r}-\mathbf{r}'|}. \tag{2}$$

The electric potential φ is given by

$$\varphi = \sum\frac{Z_i}{r_i} - \int\frac{\rho(\mathbf{r}')\,dv'}{|\mathbf{r}-\mathbf{r}'|}, \tag{3}$$

$$\nabla^2\varphi = -4\pi\sum Z_i\delta(\mathbf{r}-\mathbf{r}_i) + 4\pi\rho. \tag{4}$$

It follows from Eq. (2) that

$$\varphi_0 = \lambda\rho_0^{2/3}, \tag{5}$$

$$\nabla^2\varphi_0 = -4\pi\sum Z_i\delta(\mathbf{r}-\mathbf{r}_i) + 4\pi\lambda^{-3/2}\varphi_0^{3/2}. \tag{6}$$

Equation (6) is the Thomas-Fermi equation for an arbitrary number of nuclei (for a neutral system no subsidiary condition is needed in performing the variation).

If the solution of Eq. (2) is found, then it can be used to simplify $H = H_0$,

$$H_0 = \frac{\lambda}{10}\int\rho_0^{5/3}\,dv - \frac{1}{2}\int\sum\frac{Z_i}{r_i}\rho_0 dv. \tag{7}$$

If $\rho = \rho_0 + \delta\rho$, $\delta\rho \ll \rho_0$, then from Eq. (2) we obtain

$$H = H_0 + \frac{1}{3}\lambda\int\rho_0^{-1/3}(\delta\rho)^2\,dv + \frac{1}{2}\iint\frac{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')\,dvdv'}{|\mathbf{r}-\mathbf{r}'|}. \tag{8}$$

From Eq. (8) it is seen that what is added to H_0 is essentially positive, so that H_0 is the minimum value of H. We note that $H_0 < 0$. This can be seen by inserting Eq. (2) into Eq. (7), obtaining

$$H_0 = -\frac{2}{5}\int\sum\frac{Z_i}{r_i}\,\rho_0 dv - \frac{1}{10}\iint\frac{\rho_0(\mathbf{r})\,\rho_0(\mathbf{r}')dvdv'}{|\mathbf{r}-\mathbf{r}'|} \tag{9}$$

$$H_0 = -\frac{2}{5}\int \lambda\rho_0^{5/3}dv - \frac{1}{2}\int \frac{\rho_0(\mathbf{r}')\,\rho_0(\mathbf{r})\,dv\,dv'}{|\mathbf{r}-\mathbf{r}'|}\,. \qquad (10)$$

2. MAXIMIZATION PRINCIPLE

Let us now consider another functional of some function f, namely

$$H_1 = -\frac{1}{4\pi}\int\left[\frac{1}{2}\,(\nabla f)^2 + \frac{8\pi}{5\lambda^{3/2}}\left(\sum\frac{Z_i}{r_i} - f\right)^{5/2}\right]dv\,. \qquad (11)$$

We shall consider only real H_1, so that $f < \sum Z_i/r_i$ (this inequality may involve some other external potential on the right side), and shall require f to vanish at infinity.* Finally, we shall take the positive root for $(\ldots)^{5/2}$. Then clearly $H_1 < 0$ and can take on arbitrarily large negative values depending on f.

The maximum value of H_1 is given by the condition

$$\delta H_1 = 0, \qquad (12)$$

which leads to the following equation for $f = f_0$:

$$\nabla^2 f_0 + 4\pi\lambda^{-3/2}\left(\sum(Z_i/r_i) - f_0\right)^{3/2} = 0. \qquad (13)$$

Now let $f = f_0 + \delta f$, $\delta f \ll f_0$. Then

$$H_1 = H_{10}$$
$$-\frac{1}{4\pi}\int\left[(\nabla f_0\cdot\nabla\delta f) - 4\pi\lambda^{-3/2}\left(\sum\frac{Z_i}{r_i} - f_0\right)^{3/2}\delta f\right]dv$$
$$-\frac{1}{4\pi}\int\left[\frac{1}{2}(\nabla\delta f)^2 + 3\pi\lambda^{-3/2}\left(\sum\frac{Z_i}{r_i} - f_0\right)^{1/2}(\delta f)^2\right]dv. \qquad (14)$$

Since

$$\int(\nabla f_0\cdot\nabla\delta f_0)\,dv = \int\nabla(\nabla f_0\cdot\delta f)\,dv - \int\nabla^2 f_0\cdot\delta f\,dv.$$

the first integral on the right side can be replaced by a surface integral at infinity and vanishes in view of the conditions on f and δf. Therefore the second term in (14) becomes

$$\frac{1}{4\pi}\int\left[\nabla^2 f_0 + 4\pi\lambda^{-3/2}\left(\sum\frac{Z_i}{r_i} - f_0\right)^{3/2}\right]\delta f\,dv$$

and vanishes in view of Eq. (13). Thus the addition to H_{10} [*i.e.*, the last term in Eq. (14)] is essentially negative, so that when we set $f = f_0$ the value of H_1 is indeed maximal.

The function $\sum(Z_i/r_i) - f_0$, as is easily seen from Eq. (13), satisfies

$$\nabla^2\left(\sum\frac{Z_i}{r} - f_0\right) = -4\pi\sum Z_i\delta(\mathbf{r}-\mathbf{r}_i) + 4\pi\lambda^{-3/2}\left(\sum\frac{Z_i}{r_i} - f_0\right)^{3/2}, \qquad (15)$$

which is identical with Eq. (6) for $\varphi_0(\mathbf{r})$. Since the boundary conditions for $\varphi_0(\mathbf{r})$ (that is, vanishing at infinity) are the same as those for $(\sum Z_i/r_i - f_0)$, we have

$$\sum Z_i/r_i - f_0 = \varphi_0. \qquad (16)$$

From (3) and (5) it follows that

$$f_0 = \int\frac{\rho_0(\mathbf{r}')\,dv'}{|\mathbf{r}-\mathbf{r}'|} = \sum\frac{Z_i}{r_i} - \lambda\rho_0^{2/3},\quad \nabla^2 f_0 = -4\pi\rho_0. \qquad (17)$$

From Eq. (11) H_1 can be written in the form

$$H_1 = \frac{1}{8\pi}\int f\nabla^2 f\,dv - \frac{2}{5}\int\left(\sum\frac{Z_i}{r_i} - f\right)^{5/2}\lambda^{-3/2}dv. \qquad (18)$$

Inserting $f = f_0$ and using Eq. (17), *i.e.*,

$$\nabla^2 f_0 = -4\pi\rho_0,\quad f_0 = \sum\frac{Z_i}{r_i} - \lambda\rho_0^{2/3},$$

we have

$$H_{10} = -\frac{1}{2}\int\left(\sum\frac{Z_i}{r_i} - \lambda\rho_0^{2/3}\right)\rho_0\,dv - \frac{2}{5}\lambda\int\rho_0^{5/3}\,dv$$
$$= \frac{\lambda}{10}\int\rho_0^{5/3}\,dv - \frac{1}{2}\int\sum\frac{Z_i}{r_i}\,\rho_0\,dv = H_0, \qquad (19)$$

which is the same as H_0 as given by Eq. (7). Thus H_0 is the absolute minimum for H and the absolute maximum for H_1.

If $f \neq f_0$, then $H_1 < H_0$. The function f can be associated in an arbitrary way with ρ, so long as Eq. (17) is satisfied in the limiting case $f \to f_0$ and $\rho \to \rho_0$. For instance, we may set

$$f = a\int\frac{\rho(\mathbf{r}')\,dv'}{|\mathbf{r}-\mathbf{r}'|} + (1-a)\left(\sum\frac{Z_i}{r_i} - \lambda\rho_0^{2/3}\right),$$

where a is an arbitrary constant.

3. ON THE PHYSICAL MEANING OF THE MINIMAL AND MAXIMAL VARIATIONAL PRINCIPLES

As is well known, Eq. (1) for H is an approximation for the quantum mechanical H given by

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*If $f = \sum Z_i/r_i$, then $H_1 = -\infty$.

$$e^{-2}H = \frac{\hbar^2}{2me^2}\int\sum_k |\nabla_k\Psi|^2\prod_k dv_k - \int\sum_k\sum_i \frac{Z_i}{r_{ik}}|\Psi|^2\prod_k dv_k + \frac{1}{2}\int\sum_{k\neq k'}\frac{|\Psi|^2}{r_{kk'}}\prod_k dv_k \tag{20}$$

(summation and multiplication are over k from 1 to ΣZ_i).

In Eq. (20) H is the mathematical expectation value of the system for arbitrary Ψ. The requirement that H be an extremum in Eq. (20) leads to one of the possible energy values of the system given by the Schrödinger equation. Only for the ground state (with minimum energy) and for electrons satisfying the Pauli exclusion principle, however, does Eq. (20) reduce approximately to Eq. (1) with $\rho = \rho_0$. If $\rho \neq \rho_0$, Eq. (1) can hardly be considered the energy of the system without additional assumptions, since a given ρ does not in general determine the Ψ function. Nevertheless, the variational principle for Eq. (1) is a consequence of the general variational principle for (20), since the relation between the kinetic energy and the density, as well as the relation between the last terms of Eqs. (1) and (20) is satisfied not only by the ground-state Ψ.

As for the maximization principle for H_1 defined by Eq. (11), the physical meaning of the f function depends on the way f is associated with the density ρ, and as has already been mentioned, this association is to some extent arbitrary. Thus although when $\rho \neq \rho_0$ we may somewhat conventionally call H as defined by Eq. (1) the energy of the system, when $f \neq f_0$ it is hardly possible to assign any physical meaning to H_1 as defined by Eq. (11).

Nevertheless, the existence of a maximization principle for H_1 and a minimization principle for H makes it possible to establish both a lower and upper bound for H_0. In order actually to calculate the exact value of $H = H_0 = H_1$, it is necessary to solve either the nonlinear integral equation (2) or the nonlinear differential equation (6), which even for two nuclei presents great calculational difficulties even with the use of an electronic computer. The functional close to the extremum is not very sensitive to small variations in the function on which it depends. Making use of this fact we may vary ρ over a more or less well chosen class of functions, obtaining an approximate value for H_0 by requiring that H be a minimum for this class. However even this operation involves calculations which are too ponderous in view of the complexity of Eq. (1). Several authors[1] have calculated H for two centers with $\rho = \rho_{01}(r_1) + \rho_{02}(r_2)$ (Hund[1] has performed the same calculation with a more complicated function for the special cases of N_2 and F_2). In all of these cases the only accurate assertion possible is that "H_0 is less than the calculated value of H." How much less, one can only guess. We now have available another accurate assertion: "H_0 is greater than the calculated value of H_1." Thus if we set $H_0 \approx (H + H_1)/2$, the error in H_0 is no greater than $\pm (H - H_1)/2$.

4. THE TWO-CENTER PROBLEM

Let us evaluate the possible error in calculating H_0 by using $\rho = \rho_{01}(r_1) + \rho_{02}(r_2)$ in H, where ρ_{01} and ρ_{02} are the solutions of Eq. (2) for each atom separately.

In view of Eq. (2) we have

$$\int\frac{\rho_{0i}(\mathbf{r}')\,dv'}{|\mathbf{r}-\mathbf{r}'|} = \frac{Z_i}{r_i} - \lambda\rho_{01}^{2/3}(r_i). \tag{21}$$

Inserting (21) into Eq. (1) we obtain

$$H = \lambda\int\left[\frac{3}{5}(\rho_{01}+\rho_{02})^{2/3} - \frac{1}{2}(\rho_{01}^{2/3}+\rho_{02}^{2/3})\right](\rho_{01}+\rho_{02})\,dv - \frac{1}{2}\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}\right)(\rho_{01}+\rho_{02})\,dv. \tag{22}$$

In order now to obtain an expression for H_1, let us set, analogously, $f = f_{01}(r_1) + f_{02}(r_2)$, where f_{01} and f_{02} are solutions of Eq. (13) for each atom separately.

Then in view of Eq. (17) we have

$$f_{0i} = Z_i/r_i - \lambda\rho_{0i}^{2/3}; \qquad \frac{1}{4\pi}\nabla^2 f_{0i} = -\rho_{0i}. \tag{23}$$

Inserting $f = f_{01} + f_{02}$ into (18) and making use of Eq. (23), we obtain

$$H_1 = \lambda\int\left[\frac{1}{2}(\rho_{01}+\rho_{02}) - \frac{2}{5}(\rho_{01}^{2/3}+\rho_{02}^{2/3})^{3/2}\right](\rho_{01}^{2/3}+\rho_{02}^{2/3})\,dv - \frac{1}{2}\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}\right)(\rho_{01}+\rho_{02})\,dv. \tag{24}$$

In order to compare (22) and (24), it is convenient to introduce the quantity

$$\alpha = (\rho_{01}-\rho_{02})/(\rho_{01}+\rho_{02}), \quad -1 < \alpha < 1. \tag{25}$$

Then

$$H = \int \xi(\alpha) \frac{1}{2} (\lambda \rho_{01}^{2/3} + \lambda \rho_{02}^{2/3}) (\rho_{01} + \rho_{02})\, dv - \frac{1}{2} \int \left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right) (\rho_{01} + \rho_{02})\, dv, \tag{26}$$

$$H_1 = \int \eta(\alpha) \frac{1}{2} (\lambda \rho_{01}^{2/3} + \lambda \rho_{02}^{2/3}) (\rho_{01} + \rho_{02})\, dv - \frac{1}{2} \int \left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right) (\rho_{01} + \rho_{02})\, dv, \tag{27}$$

where

$$\xi(\alpha) = 1.2 \left[\left(\frac{1+\alpha}{2} \right)^{2/3} + \left(\frac{1-\alpha}{2} \right)^{2/3} \right]^{-1} - 1, \qquad \eta(\alpha) = 1 - 0.8 \left[\left(\frac{1+\alpha}{2} \right)^{2/3} + \left(\frac{1-\alpha}{2} \right)^{2/3} \right]^{3/2}. \tag{28}$$

Some values of $\xi(\alpha)$ and $\eta(\alpha)$ are given in the following table: Clearly, ξ and η are even functions of α.

α	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
ξ	−0.048	−0.047	−0.044	−0.038	−0.028	−0.017	−0.002	+0.016	0.042	0.090	0.200
η	−0.132	−0.129	−0.124	−0.115	−0.101	−0.084	−0.061	−0.031	+0.008	+0.074	0.200
$\xi - \eta$	0.084	0.082	0.080	0.077	0.073	0.067	0.059	0.047	0.034	0.016	0.000

We now note that according to (21)

$$\varphi_{01} = \lambda \rho_{01}^{2/3} < Z_1 / r_1, \quad \varphi_{02} = \lambda \rho_{02}^{2/3} < Z_2 / r_2. \tag{29}$$

Therefore

$$\int \frac{1}{2} (\lambda \rho_{01}^{2/3} + \lambda \rho_{02}^{2/3}) (\rho_{01} + \rho_{02})\, dv < \frac{1}{2} \int \left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right) (\rho_{01} + \rho_{02})\, dv. \tag{30}$$

Since the absolute values of ξ and η are no greater than 0.2, the last integral in both Eqs. (26) and (27) is at least five times greater than the first integrals in these equations. Therefore the last integrals in (26) and (27) effectively determine the magnitudes of H and H_1, and therefore also of H_0. From Eq. (30) and the table for ξ and η,

$$H - H_1 < 0{,}084 \int \frac{1}{2} (\lambda \rho_{01}^{2/3} + \lambda \rho_{02}^{2/3}) (\rho_{01} + \rho_{02})\, dv$$

$$< 0{,}08 \int \left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2} \right) (\rho_{01} + \rho_{02})\, dv,$$

since $\xi - \eta \leqslant 0.084$. Therefore H differs from H_0 by no more than +8% and the mean $(H + H_1)/2$ differs from H_0 by no more than 4%.

We have determined here the upper limit of the error, which is actually much smaller. In order to calculate it, H and H_1 must be calculated with the appropriate Z_1 and Z_2 and with the nuclear separation R. The value of $\xi - \eta$ is about 0.08 only if $\rho_{01} \approx \rho_{02}$, and is smaller in all other cases. Therefore $H - H_1$ becomes larger as Z_2 and Z_1 approach each other, and as R becomes smaller. In the limit $Z_2 = Z_1$ and $R = 0$, the calculation of H and H_1 is simply performed (since this case $\rho_{01} = \rho_{02}$) using the well known relations

$$\frac{3}{5} \lambda \int \rho_{0i}^{5/3}\, dv = -H_{0i} = C \frac{Z_i^{7/3}}{\lambda}; \qquad \int \frac{Z_i}{r_i} \rho_{0i}\, dv = \frac{7}{3} C \frac{Z_i^{7/3}}{\lambda}.$$

$$H = -0.048 \cdot 2 \int \lambda \rho_{01}^{5/3}\, dv - 2 \int \frac{Z_1}{r_1} \rho_{01}\, dv = -4.83\, C \frac{Z_1^{7/3}}{\lambda},$$

$$H_1 = -0.132 \cdot 2 \int \lambda \rho_{01}^{5/3}\, dv - 2 \int \frac{Z_1}{r_1} \rho_{01}\, dv = -5\ 11\, C \frac{Z_1^{7/3}}{\lambda}.$$

When $Z_2 = Z_1$ we must set $Z = 2Z_1$ in H_0, so that

$$H_0 = -2^{7/3}CZ_1^{7/3}/\lambda = -5.04CZ_1^{7/3}/\lambda.$$

Thus

$$\frac{H-H_0}{H_0} = 4.17\%, \quad \frac{H_0-H_1}{H_0} = 1.38\%,$$

$$\frac{{}^1/_2(H+H_1)-H_0}{H_0} = 1.38\%.$$

[1] P. Gombas, *Statistical Theory of the Atom and its Applications,* (Russian translation of *Statistische Theorie des Atoms und Ihre Anwendungen,* Springer-Verlag, Vienna, 1949).IIL, Moscow, 1951.

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On the Exciton Mechanism for Capture of Current Carriers in Homopolar Semiconductors

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Capture of charge carriers by structural defects, in which energy is transferred to small radius excitons, is investigated. The temperature dependence of recombination coefficients is determined.

1. INTRODUCTION

THE PROBLEM OF THE MECHANISM for capture of current carriers by impurity centers is still unsolved. This statement is particularly applicable to the mechanism for carrying off the energy which is liberated during the localization of a carrier which makes a transition from a band to an impurity level. Until recently it was implicitly assumed that this energy is given directly to the lattice, which undergoes a deformation during an electron transition of this type. Only recently it has been shown[1-4] that this possibility is by no means the only one, and that the so-called radiationless transitions can (at least, in their first stage) also proceed without participation by the lattice, but rather via a redistribution of the energy within the many-electron system itself. In Refs. 1 – 3 this redistribution was caused by the presence of another carrier, to which the liberated energy was transferred. Reference 4 pointed out that for a radiationless transition it is sufficient for the energy to be transferred to any neutral excitation of the many-electron system, and treated the process of capture with excitation of plasma oscillations. In all these cases, the conversion of the excitation energy into heat (*i.e.*, conversion into phonons) occurs only in a later, much slower stage of the process.

In the present paper we shall treat the "exciton" mechanism for capture, in which the liberated energy goes into the formation of "Frenkel excitons" (*i.e.*, excitons of small radius and, consequently, rather high dissociation energy). The inverse process – the ionization of impurity centers by exciton impact – was discussed earlier by Lashkarev[5] and Zhuze and Ryvkin,[6] and treated quantitatively by Toyozawa[7] (*cf.* also Ref. 18). However, there are various contradictory points in Ref. 7. In the first place, in the formulation of the problem given there, the interaction of the electrons with the exciton field is not at all small, whereas a weak coupling method is used in the calculation. In addition, even if we disregard this main objection, the specific computations in Ref. 7 are applicable only to traps which are sufficiently shallow to be described by the "hydrogen" model. All of these considerations have compelled us once again to consider the exciton mechanism for capture, using for this purpose the consistent many-electron theory of semiconductors developed earlier.[8] In accordance with many well known experimental results, we shall consider the capture of current carriers by deep traps. Calculation of the absolute value of the capture cross section turns out to be extremely difficult; however, its temperature dependence can be determined quite well, as we shall show later.

In order to emphasize the essentially "intra-elec-