Commun. Math. Phys. 81, 419–428 (1981)

Communications in Mathematical Physics

Dependence of the Thomas-Fermi Energy on the Nuclear Coordinates*

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Abstract. Let $E(R)$, respectively $e(R)$, denote the total energy, respectively the electronic contribution to the energy, in the Thomas-Fermi theory for a system of two fixed nuclei a distance R apart. We prove that $e(R)$ and $-E(R)$ increase as R does. For the case of N fixed nuclei, we prove the monotonicity of e and E under certain displacements of the coordinates of the nuclei. The analogous result for the electronic contribution to the Born-Oppenheimer energy is proved.

1. Introduction

The Thomas-Fermi (TF) theory is defined by the energy functional (in units in which $h^2(8m)^{-1}(3/\pi)^{2/3}=1$ and $|e|=1$, where e and m are the electron charge and mass)

$$\xi(\rho)=\tfrac{3}{5}\int \rho(x)^{5/3}\,dx-\int V(x)\,\rho(x)\,dx+D(\rho,\rho)+U, \tag{1}$$

where

$$D(\rho,\rho)\equiv\tfrac{1}{2}\int \rho(x)\,|x-y|^{-1}\,\rho(y)\,dx\,dy, \tag{2}$$

$$V(x)=\sum_{j=1}^{k} z_j|x-R_j|^{-1}, \tag{3}$$

and

$$U=\sum_{1\leqq i<j\leqq k} z_i z_j\,|R_i-R_j|^{-1}. \tag{4}$$

Here $z_1,\dots,z_k\geqq 0$ are the charges of k fixed nuclei located at $R_1,\dots,R_k$. $\int dx$ is always a three-dimensional integral. $\xi(\rho)$ is defined for electronic densities $\rho(x)\geqq 0$ such that $\int\rho$ and $\int\rho^{5/3}$ are finite. The TF energy for λ (not necessarily an integer) electrons is defined by

$$E(\lambda;\{R_i\})=\inf\{\xi(\rho)\,|\,\int\rho=\lambda\}. \tag{5}$$

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* Research supported by U.S. National Science Foundation under Grant MCS 80-17781

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0010-3616/81/0081/0419/$02.00

It is known [1] that for $\lambda \leqq Z \equiv \sum_{j=1}^{k} z_j$ there is a unique minimizing ρ for (5). It is the unique solution to the TF equation

$$\rho(x)^{2/3} = \max(\phi(x) - \phi_0, 0) \tag{6}$$

for some $\phi_0 \geqq 0$ and with

$$\phi(x) \equiv V(x) - \int \rho(y)|x-y|^{-1}\, dy. \tag{7}$$

$-\phi_0$ is the chemical potential, i.e.,

$$\frac{dE}{d\lambda}(\lambda; \{R_i\}) = -\phi_0. \tag{8}$$

For $\lambda \leqq Z$, $\phi(x) > 0$, all x. $\phi_0 = 0$ if and only if $\lambda = Z$. If $\lambda > Z$, there is no minimizing ρ for (5), and $E(\lambda; \{R_i\}) = E(Z; \{R_i\})$ in this case.

Let us denote by

$$e(\lambda; \{R_i\}) \equiv E(\lambda; \{R_i\}) - U \tag{9}$$

the electronic contribution to the TF energy. In this article we study the dependence of both $E(\lambda; \{R_i\})$ and $e(\lambda; \{R_i\})$ on the nuclear coordinates $R_1, \ldots, R_k$. We will start by indicating some of the previously obtained results concerning this dependence:

(i) It was proven by Teller [2] that for fixed $\lambda \leqq Z$ the TF energy $E(\lambda; \{R_i\})$ is greater than the TF energy for isolated atoms (i.e., the energy when the R_i are infinitely far apart). A stronger result has been proven [3] for neutral systems, i.e., for $\lambda = Z$, namely $E(\lambda; \{R_i\})$ decreases under dilation, $R_i \to \ell R_i$ ($\ell > 1$), all $1 \leqq i \leqq k$. It has been conjectured [3], but not yet proven, that this should also hold for the subneutral case (i.e., for $\lambda < Z$).

(ii) As for the electronic contribution to the energy, it is an elementary consequence of the concavity of $e(\lambda; \{R_i\})$ on the nuclear charges z_i that, for fixed λ and z_i, $1 \leqq i \leqq k$, $e(\lambda; \{R_i\})$ always takes its minimum value when all R_i are equal ([1], Theorem V.4). (This property also holds for the electronic contribution to the Born-Oppenheimer energy ([4], [5], Theorem 3)). Lieb and Simon ([1], Theorem V.3) proved that $e(\lambda; \{R_i\})$ is smaller than the corresponding e when the R_i are infinitely apart. A stronger result has been conjectured [3] namely, $e(\lambda; \{R_i\})$ should increase under dilations $R_i \to \ell R_i$, $\ell \geqq 1$, all $1 \leqq i \leqq k$, for any fixed $\lambda \leqq Z$.

There are other interesting results concerning the dependence of e and E on the nuclear coordinates (see [3], [6]), but they are not relevant for our discussion here. For a review see [7], (Sect. IV).

The main result of this article is

Theorem 1. *Fix z_i, all $1 \leqq i \leqq k$, and $\lambda (\leqq Z)$. Fix j ($1 \leqq j \leqq k$) and assume that R_j is such that*

$$R_i \in \{x \in \mathbb{R}^3 \,|\, (x - R_j) \cdot n \leqq 0\}, \quad \text{all } i \neq j$$

for some fixed $n \in \mathbb{R}^3$. *Define* $E(\lambda;\alpha) \equiv E(\lambda;\{R_1,\ldots,R_{j-1},R_j+\alpha n, R_{j+1},\ldots,R_k\})$ *and* $e(\lambda;\alpha) \equiv e(\lambda;\{R_1,\ldots,R_{j-1},R_j+\alpha n, R_{j+1},\ldots,R_k\})$. *Then*

(i) $E(\lambda;\alpha)$ *is a monotonic non-increasing function of* $\alpha \geqq 0$,

(ii) $e(\lambda;\alpha)$ *is a monotonic non-decreasing function of* $\alpha \geqq 0$,

(iii) *for fixed* $\alpha > 0$, $E(\lambda;\alpha) - E(\lambda;0)$ *is non-decreasing in* λ,

(iv) *for fixed* $\alpha > 0$, $e(\lambda;\alpha) - e(\lambda;0)$ *is non-decreasing in* λ. *(Hereafter* $x \cdot y$ *will denote the usual inner product in* $\mathbb{R}^3$.*)*

Remarks. (i) The essential content of this Theorem is the following. Let $R_1,\ldots,R_k$ be given and let C be their convex hull. C has a surface S which is a (possibly degenerate) polyhedron whose vertices are $R_1,R_2,\ldots,R_n$, say. Now consider any displacement of $R_1,\ldots,R_n$ (and not the other R's) which has the property that $|R_i'-R_j'| \geqq |R_i-R_j|$ for *all* i,j then E decreases and e increases. Furthermore, if $\lambda_1 < \lambda_2$, then the decrease (increase in $E(e)$ is smaller (larger) for λ_2 than for λ_1. (Here R_i' denote the new coordinates of the nuclei after the displacement.)

(ii) Note that Theorem 1, (i), (ii) hold for any $\lambda \leqq Z$ and not just for neutral systems.

(iii) For certain nuclear configurations, it follows from Theorem 1, (ii) that $e(\lambda;\{R_i\})$ is not decreased under dilations $R_i \to \ell R_i$, $\ell \geqq 1$, all i (as well as under other displacements of the nuclei). This verifies the (still open) conjecture 4 of [3] for these nuclear configurations.

(iv) In the Born-Oppenheimer approximation, in the case of one electron and N nuclei, the electronic contribution to the energy is monotonic non-decreasing under dilations $R_i \to \ell R_i$, $(\ell \geqq 1)$, all i ([5], Theorem 2). We prove below (Sect. 4) that the analog of Theorem 1 (ii) in the Born-Oppenheimer approximation also holds.

In Sect. 2 we introduce, for technical reasons, a regularized TF model. In Sect. 3 we prove Theorem 1 for this regularized TF, and using the convergence of the regularized TF energy to the TF energy, we prove Theorem 1. Finally in Sect. 4 we prove the analog of Theorem 1, (ii) for the Born-Oppenheimer electronic energy.

2. A Regularized TF Theory

Let g be a non-negative real-valued function belonging to $C_0^\infty(\mathbb{R}^+)$ and having the properties

(i) $g(r) = 0 \quad$ if $r \geqq 1$,

(ii) $4\pi \int_0^\infty g(r) r^2\,dr = 1$,

(iii) $g(r)$ is a decreasing function of r.

For $a > 0$, let $g_a(x) \equiv a^{-3} g(|x|/a)$, $x \in \mathbb{R}^3$. For $0 < a < \min\{|R_i - R_j| \,|\, 1 \leqq i < j \leqq k\}$, define

$$V_a(x) = (g_a * V)(x), \tag{10}$$

(i.e., V_a is the Coulomb potential corresponding to smeared nuclei; we have imposed an upper bound on a so that the smeared nuclei do not overlap). Since $V \in L^1_{\text{loc}}$, $V_a \in C^\infty(\mathbb{R}^3)$.

Let us define a regularized TF theory by the functional

$$\xi_a(\rho; \{R_i\}) = \tfrac{3}{5} \int \rho(x)^{5/3}\, dx - \int V_a(x)\, \rho(x)\, dx + D(\rho, \rho) + U_a, \tag{11}$$

with

$$U_a = U_a(\{R_i\}) \equiv \sum_{1 \leqq i < j \leqq k} z_i z_j \iint dy\, dx\, g_a(x)\, g_a(y)\, |x - R_i - y + R_j|^{-1}. \tag{12}$$

That is, the functional $\xi_a(\rho; \{R_i\})$ is of exactly the same form as the TF functional $\xi(\rho)$, given by (1), the only change being in that we have smeared the singularities of $V(x)$. (Note that we have also changed the constant term U by U_a which represents the interaction between the smeared nuclei.)

The minimization problem associated with $\xi_a(\rho)$ is contained in the family of variational principles studied in Refs. [1] and [8]. We summarize below those properties of this regularized TF theory that we will need in the sequel:

(i) The problem $\operatorname{Min}\{\xi_a(\rho) \mid \rho \in L^1 \cap L^{5/3},\ \rho(x) \geqq 0,\ \int \rho(x)\, dx = \lambda\}$, has a unique solution for $0 \leqq \lambda \leqq Z$. For $\lambda > Z$ there is no solution. (That Z is the largest λ for which there is a solution follows from [8], Theorem 3 (c), since

$$\int (-\Delta V_a) = \int (-\Delta V_a)_+ = \sum_{i=1}^{k} z_i = Z.)$$

(ii) The unique minimizing ρ_a satisfies the Euler equation

$$\rho_a^{2/3}(x) = \max(\phi_a(x) - \phi_0, 0), \tag{13}$$

for some $\phi_0 \geqq 0$, where

$$\phi_a(x) \equiv V_a(x) - \int dy\, \rho_a(y)\, |x - y|^{-1}. \tag{14}$$

(iii) $\phi_a(x)$ and thus $\rho_a(x)$ are continuous everywhere and they go to zero at infinity. (This follows from (14), since $V_a(x)$ is continuous everywhere and goes to zero at infinity and so does $\rho_a * |x|^{-1}$ (see [1], Theorem II.25) because $\rho_a \in L^{5/3} \cap L^1$ and $|x|^{-1} \in L^{5/2} + L^4$.)

Let us define the total energy of the regularized TF theory by

$$E_a(\lambda; \{R_i\}) \equiv \min\{\xi_a(\rho; \{R_i\}) \mid \textstyle\int \rho = \lambda\},$$

and the corresponding electronic contribution by

$$e_a(\lambda; \{R_i\}) \equiv E_a(\lambda; \{R_i\}) - U_a(\{R_i\}).$$

We are interested in the dependence of E_a and e_a on the nuclear coordinates; in particular let us keep $R_2, \ldots, R_k$ fixed and study the change on E_a and e_a under the shift $R_1 \to R_1 + \alpha n$, with $\alpha \geqq 0$, $n \in \mathbb{R}^3$. Denote by $E_a(\lambda; \alpha) \equiv E_a(\lambda; \{R_1 + \alpha n, R_2, \ldots, R_k\})$ and $e_a(\lambda; \alpha) \equiv e_a(\lambda; \{R_1 + \alpha n, R_2, \ldots, R_k\})$. Let V^α be given by (3) with R_1 replaced by $R_1 + \alpha n$ and $V_a^\alpha \equiv g_a * V^\alpha$. We have the following

Theorem 2. *(A Feynman-Hellman theorem for regularized* TF.*) Let ρ^α be the unique minimizing ρ for $\xi_a(\cdot\,;\{R_i\}^\alpha)$ with $\int\rho^\alpha=\lambda$. (Here we have used $\{R_i\}^\alpha$ to denote $\{R_1+\alpha n, R_2, \dots, R_k\}$.) Then,*

(i) *The functions $\alpha\to E_a(\lambda;\alpha)$ and $\alpha\to e_a(\lambda;\alpha)$ are continuously differentiable and*

$$\text{(ii)}\quad \partial e_a/\partial\alpha=-\int \partial V_a^\alpha/\partial\alpha(x)\,\rho^\alpha(x)\,dx \tag{15}$$

$$=z_1\int[n\cdot\nabla g_a(y)]\,\psi^\alpha(y+R_1+\alpha n)\,dy, \tag{16}$$

$$\text{(iii)}\quad \partial E_a/\partial\alpha=-z_1\int[n\cdot\nabla g_a(y)]\,\phi^\alpha(y+R_1+\alpha n)\,dy, \tag{17}$$

where $\psi^\alpha\equiv\rho^\alpha * |x|^{-1}$ and $\phi^\alpha\equiv V_a^\alpha-\psi^\alpha$.

Proof. Let us first prove that the mapping $\alpha\to\int\partial V_a^\alpha/\partial\alpha(x)\,\rho^\alpha(x)\,dx$ is continuous. We need only prove continuity at $\alpha=0$. Note that $V_a^\alpha\to V_a$ in $L^{5/2}+L^4$ (Lemma A.1), and therefore $\rho^\alpha\to\rho^0$ in $L^{5/3}$ because of Theorem II.15 in [1]. Since $\|\rho^\alpha\|_1\leqq\lambda$, we also have $\rho^\alpha\to\rho^0$ in (weak) L^p, any $1<p<5/3$. Let $Y^\alpha\equiv\partial V_a^\alpha/\partial\alpha$, we have

$$\int Y^\alpha\rho^\alpha-\int Y^0\rho^0=\int(Y^\alpha\rho^\alpha-Y^0\rho^\alpha)+\int(Y^0\rho^\alpha-Y^0\rho^0). \tag{18}$$

The first term in the right side of (18) goes to zero as $\alpha\downarrow 0$ because $Y^\alpha\to Y^0$ in $L^{5/2}+L^4$ and ρ^α is bounded in $L^{5/3}\cap L^{4/3}$. Also $\int Y^0(\rho^\alpha-\rho^0)\to 0$, as $\alpha\downarrow 0$, because $Y^0\in L^{5/2}+L^4$ and $\rho^\alpha\to\rho^0$ in $L^{5/3}$ and $\rho^\alpha\to\rho^0$ in (weak) $L^{4/3}$, hence $\alpha\to\int\partial V_a^\alpha/\partial\alpha(x)\,\rho^\alpha(x)\,dx$ is continuous.

Now, we prove differentiability of e_a. Again we need only prove it at $\alpha=0$. For $\alpha>0$,

$$\begin{aligned}\alpha^{-1}[e_a(\lambda;\alpha)-e_a(\lambda;0)]&\leqq\alpha^{-1}\{[\xi_a(\rho^0;\{R_i\}^\alpha)-U_a(\{R_i\}^\alpha)]\\&-[\xi_a(\rho^0;\{R_i\})-U_a(\{R_i\})]\}=-\int\alpha^{-1}(V_a^\alpha-V_a)(x)\,\rho^0(x)\,dx,\end{aligned} \tag{19}$$

by the minimization property of ρ^α. By the minimization property of ρ^0

$$\alpha^{-1}[e_a(\lambda;\alpha)-e_a(\lambda,0)]\geqq-\int\alpha^{-1}(V_a^\alpha-V_a)(x)\,\rho^\alpha(x)\,dx. \tag{20}$$

Now, $\alpha^{-1}[V_a^\alpha-V_a]\to\partial V_a^\alpha/\partial\alpha|_{\alpha=0}$ in $L^{5/2}+L^4$ (see Lemma A.2 in the Appendix) and $\rho^0\in L^{5/3}\cap L^1$ hence, by Hölder's inequality, the right side of (19) converges to $-\int\partial V_a^\alpha/\partial\alpha|_{\alpha=0}(x)\,\rho_0(x)\,dx$ as $\alpha\downarrow 0$. Similarly, one can prove that the right side of (20) converges to the same limit as $\alpha\downarrow 0$ and, therefore,

$$\lim_{\alpha\downarrow 0}\alpha^{-1}[e_a(\lambda;\alpha)-e_a(\lambda;0)]=-\int\left.\frac{\partial V_a^\alpha}{\partial\alpha}\right|_{\alpha=0}(x)\,\rho^0(x)\,dx. \tag{21}$$

A similar argument controls $\lim_{\alpha\uparrow 0}$. Thus $e_a(\lambda;\alpha)$ is continuously differentiable in α and its derivative is given by (15). In order to prove (16), we just compute $\partial V_a^\alpha/\partial\alpha(x)=z_1\int g_a(y)\,n\cdot\nabla_y|x-y-R_1-\alpha n|^{-1}\,dy$, and after introducing this expression in (15), we integrate by parts. Finally, since $U_a(\{R_i\}^\alpha)$ is continuously differentiable with respect to α (see Lemma A.3), $\alpha\to E_a(\lambda;\alpha)$ is continuously differentiable. Moreover,

$$\frac{\partial U_a(\{R_i\}^\alpha)}{\partial \alpha} = -z_1 \int [n \cdot \nabla g_a(y)] \, V_a^\alpha(y + R_1 + \alpha n) \, dy, \tag{22}$$

and adding the right sides of (16) and (22) we get the right side of (17). This concludes the proof of the theorem. □

3. Proof of Theorem 1

We will need some geometric preliminaries. For n, a unit vector in $\mathbb{R}^3$ and $d \geqq 0$, let $P(n,d)$ be the plane

$$P(n,d) \equiv \{x \in \mathbb{R}^3 \,|\, x \cdot n = d\},$$

and let $P^+(n,d)$ denote the open half-space

$$P^+(n,d) \equiv \{x \in \mathbb{R}^3 \,|\, x \cdot n < d\},$$

and $P^-(n,d) = \mathbb{R}^3 \setminus (P^+(n,d) \cup P(n,d))$. For any function f: $\mathbb{R}^3 \to \mathbb{R}$ we define

$$f^+(x) = f(x)$$
$$f^-(x) = f(x + 2(d - x \cdot n)\, n),$$

for every $x \in P^+(n,d) \cup P(n,d)$, i.e., f^- is just the reflection of f through the plane $P(n,d)$. In order to prove Theorem 1 we will need the following:

Lemma 3. *Let n and d be such that $R_i \in P^+(n,d) \cup P(n,d)$ for all $1 \leqq i \leqq k$ and choose $a < \min_j \{\operatorname{dist}(R_j, P(n,d)) \,|\, R_j \notin P(n,d)\}$, (this condition on a insures that the smeared nuclei with $R_i \in P^+(n,d)$ are supported on $P^+(n,d)$). Let $\rho_a(x)$ be the unique solution to the regularized* TF *equation* (13) *and ϕ_a the corresponding potential* (14). *Then*

(i) $h_a(x) \equiv \phi_a^+(x) - \phi_a^-(x) > 0$, *all* $x \in P^+(n,d)$

(ii) *For each* $x \in P^+(n,d)$, $h_a(x)$ *strictly decreases when* λ *increases, and*

(iii) $\rho_a^+(x) - \rho_a^-(x) \geqq 0$, *all* $x \in P^+(n,d)$.

Proof. (i) Certainly $h_a(x) = 0$ for $x \in \partial P^+(n,d) = P(n,d)$ and at infinity. Let $D = \{x \in P^+ \,|\, h_a(x) < 0\}$. Since ϕ_a is continuous everywhere (see Sect. 2), D is open. On D, $-(4\pi)^{-1} \Delta h_a \geqq \rho_a^- - \rho_a^+ > 0$ since, through Eq. (13), $\phi_a^- > \phi_a^+$ implies $\rho_a^- > \rho_a^+$. Thus, h_a is superharmonic on D, so D is empty. By the strong maximum principle, $h_a(x) > 0$, in fact, for $x \in P^+(n,d)$. (ii) Let $\lambda' < \lambda$ with corresponding h_a' and h_a. We want to prove that $B = \{x \in P^+ \,|\, h_a(x) - h_a'(x) > 0\}$ is empty. Since the h_a's are continuous, B is open and $h_a - h_a' = 0$ on $P(n,d)$ and at infinity. We have

$$-(4\pi)^{-1} \Delta (h_a - h_a') = -b_+^{3/2} + c_+^{3/2} + p_+^{3/2} - q_+^{3/2} \equiv r,$$

with

$$b = \phi_a^+ - \mu, \quad c = \phi_a^- - \mu, \quad p = \phi_a^{+\prime} - \mu', \quad q = \phi_a^{-\prime} - \mu', \qquad (\mu = \phi_0^{(\lambda)},\ \mu' = \phi_0^{(\lambda')}).$$

By (i) ([1], Theorem V.9), $b > c \geqq q$ and $b \geqq p > q$, for all $x \in P^+$. On B, $b + q > c + p$. Thus $r \leqq 0$ on B, whence $h_a(x) - h_a'(x)$ is subharmonic on B and therefore B

is empty. Again, once can prove the stronger result that $h_a(x)-h'_a(x)<0$ for $x\in P^+$. Trivially, (i) implies (iii) through the TF equation (13). □

Remarks. (i) The proof of Lemma 3, (i) is analogous to the proof of Teller's lemma ([1], Theorem V.8).

(ii) By the same argument once can prove the following two lemmas.

Lemma 4. *Let n and d be such that $R_i\in P^+(n,d)$ for all $1\leqq i\leqq k$ and let $\rho(x)$ be the unique solution to the* TF *equation* (6). *Then*

$$\rho^+(x)>\rho^-(x), \qquad \text{all } x\in P^+(n,d).$$

Lemma 5. *Let n and d be as in Lemma* 4. *Let V be the Coulomb potential* (3). *Then*

$$V^+(x)>V^-(x), \qquad \text{all } x\in P^+(n,d).$$

Remark. This property of V is exactly the one needed to prove Theorem 1 and 4 in [5] and Theorem 3.2 in [9].

We will now prove the analog of Theorem 1 for the regularized TF model:

Theorem 6. *Fix z_i all $1\leqq i\leqq k$ and $\lambda\leqq Z$. Fix $j\,(1\leqq j\leqq k)$ and assume that R_j is such that*

$$R_i\in P^+(n,n\cdot R_j)\cup P(n,n\cdot R_j), \qquad \text{all } i\neq j \tag{23}$$

for some fixed unit vector $n\in\mathbb{R}^3$. Let $E_a(\lambda,\alpha)\equiv E_a(\lambda;\ \{R_1,\dots,R_{j-1},\ R_j+\alpha n,\ R_{j+1},\dots,R_k\})$ and $e_a(\lambda;\alpha)\equiv e_a(\lambda;\ \{R_1,\dots,R_{j-1},\ R_j+\alpha n,\ R_{j+1},\dots,R_k\})$. Choose $a<\min_i\{\operatorname{dist}(R_i,P(n,n\cdot R_j))\,|\,R_i\notin P(n,n\cdot R_j)\}$. Then,

(i) *$E_a(\lambda;\alpha)$ is a monotonic non-increasing function of $\alpha\geqq 0$,*

(ii) *$e_a(\lambda;\alpha)$ is a monotonic non-decreasing function of $\alpha\geqq 0$,*

(iii) *for fixed $\alpha>0$, $E_a(\lambda;\alpha)-E_a(\lambda;0)$ is non-decreasing in λ,*

(iv) *for fixed $\alpha>0$, $e_a(\lambda;\alpha)-e_a(\lambda;0)$ is non-decreasing in λ.*

Proof. (i) By the Feynman-Hellman Theorem 2 [see Sect. 2, Eq. (17)],

$$\left.\frac{dE_a}{d\alpha}\right|_{\alpha=0}=-z_j\int[n\cdot\nabla g_a(y-R_j)]\,\phi_a(y)\,dy. \tag{24}$$

We can write the right side of (24) as

$$-z_j\int_{y\in\bar{P}^+(n,n\cdot R_j)}[n\cdot\nabla g_a(y-R_j)][\phi_a^+(y)-\phi_a^-(y)]\,dy, \tag{25}$$

because $n\cdot\nabla g_a(y-R_j)$ only changes sign under a reflection (of y) through $P(n,n\cdot R_j)$. Here $\phi_a^\pm$ are defined as in (23) with respect to the plane $P(n,n\cdot R_j)$. Since $n\cdot\nabla g_a(y-R_j)\geqq 0$, all $y\in P^+\cup P$ [because $g_a(y)$ is spherically symmetric and decreasing] and $\phi_a^+(y)\geqq\phi_a^-(y)$, all $y\in P^+\cup P$ [Lemma 3, (i)], (25) is non-postive and (i) follows.

(iii) Write $E_a(\lambda,\alpha)-E_a(\lambda,0)=\int_0^\alpha dE_a/d\alpha\,d\alpha$. Now, for every fixed α, $dE_a/d\alpha(\lambda,\alpha)$ is an increasing function of λ because of (25) and Lemma 3(ii).

(ii) By integration by parts one can write (15) as

$$\left.\frac{de_a}{d\alpha}\right|_{\alpha=0} = z_j \int p_j(x)\,\rho_a(x)\,dx,$$

with

$$p_j(x) \equiv n \cdot \nabla_x \int g_a(x-y)\,|y-R_j|^{-1}\,dy.$$

As before, we have

$$\left.\frac{de_a}{d\alpha}\right|_{\alpha=0} = z_j \int_{x \in \bar{P}^+(n,\, n \cdot R_j)} p_j(x)\,(\rho_a^+(x) - \rho_a^-(x))\,dx, \tag{26}$$

because $p_j(x)$ only changes sign under a reflection (of x) through $P(n, n \cdot R_j)$. Moreover, $p_j(x) \geqq 0$, all $x \in P^+ \cup P$ (because $g_a * |x-R_j|^{-1}$ is spherically symmetric and decreasing). Hence, (ii) follows from (26) and Lemma 3(iii). Finally, it should be clear that (iii) is equivalent to (iv). □

After all these preliminaries we can go to the

Proof of Theorem 1. Because of Lemma A.4, $V_a \to V$ *as* $a \downarrow 0$, *in* $L^{5/2} + L^4$. Therefore, Theorem II.15 in [1] implies that, for fixed λ, $e_a(\lambda; \{R_i\}) \to e(\lambda; \{R_i\})$ as $a \downarrow 0$. Hence Theorem 1 (ii) and (iv) follow from Theorem 6 (ii), (iv). Now, by Lemma A.5, $U_a \to U$ as $a \downarrow 0$, hence for fixed λ, $E_a(\lambda; \{R_i\}) \to E(\lambda; \{R_i\})$ as $a \downarrow 0$. Therefore Theorem 1 (i) and (iii) follow from Theorem 6 (i), (iii). □

4. Proof of Theorem 1(ii) for the Electronic Contribution to the Born-Oppenheimer Energy

The electronic contribution to the Born-Oppenheimer energy for a system of one electron and k (fixed) nuclei (located at $R_i \in \mathbb{R}^3$, with positive charge z_i) is defined by [5]:

$$e(\{R_i\}) = \inf \operatorname{spec}(H_e), \tag{27}$$

with

$$H_e = -\Delta - \sum_{i=1}^{k} z_i\,|x-R_i|^{-1}. \tag{28}$$

The behavior of $e(\{R_i\})$ as a function of the nuclear coordinates has been studied in [5] and [9]. In particular, it has been shown [5] that $e(\{R_i\})$ is monotonic non-decreasing under the dilation $R_i \to \ell R_i$ ($\ell > 1$), all i. Here we will prove the following related result:

Theorem 7. *Fix* z_i, *all* $1 \leqq i \leqq k$. *Fix* j $(1 \leqq j \leqq k)$ *and assume that* R_j *is such that*

$$R_i \in \{x \in \mathbb{R}^3 \,|\, (x-R_j) \cdot n \leqq 0\}, \qquad \textit{all } i \neq j, \tag{29}$$

for some fixed unit vector $n \in \mathbb{R}^3$. *Then* $e(\{R_1, \ldots, R_{j-1}, R_j + \alpha n, R_{j+1}, \ldots, R_k\})$ *is a monotonic non-decreasing function of* $\alpha \geqq 0$.

Remark. This is a straightforward generalization of Hoffman-Ostenhof's (Theorem 3.2, [9]) and therefore we will give here only the necessary modifications to his proof.

Proof. Because of Lemma 5 (Sect. 3) and the comparison Theorem 2.3 of [9], we have that $\psi^+(x) \geqq \psi^-(x)$, all $x \in P^+(n, n\cdot R_j)$. Here ψ^- is the reflection of the ground state ψ of H_e with respect to $P(n, n\cdot R_j)$ and $\psi^+ = \psi$. Therefore, by the Feynman-Hellman theorem we have

$$\begin{aligned}\left.\frac{de}{d\alpha}\right|_{\alpha=0} &= -z_j \int |x-R_j|^{-3}(x-R_j)\cdot n\psi^2(x)\,dx \\ &= -z_j \int_{x\in P^+(n,\, n\cdot R_j)} |x-R_j|^{-3}(x-R_j)\cdot n(\psi^+(x)^2 - \psi^-(x)^2)\,dx \\ &\geqq 0. \quad \square\end{aligned}$$

Appendix

Let $f \in (L^{5/2}+L^4)(\mathbb{R}^3, dx)$ and define $f_a(x) = (g_a * f)(x)$, with g_a given as in Sect. 2, for $a>0$. Since $f \in L^1_{\text{loc}}$, then $f_a \in C^\infty(\mathbb{R}^3)$ ([10], Lemma 2.18(a)). Moreover $f_a \in L^{5/2}+L^4$, by using Young's inequality.

Lemma A.1. (Continuity of $f_a(x)$ under translation.) *Let* $f_a^\alpha(x) \equiv f_a(x-\alpha R)$, $\alpha>0$, $R \in \mathbb{R}^3$. *Then* $f_a^\alpha \to f_a$ *in* $L^{5/2}+L^4$ *as* $\alpha \downarrow 0$.

Proof. Since $(f_a^\alpha - f_a)(x) = \int [g_a(y-\alpha R) - g_a(y)] f(x-y)\,dy$, and $g_a \in C^\infty$, we have

$$\begin{aligned}|(f_a^\alpha - f_a)(x)| &\leqq \int dy\, |f(x-y)| \int_0^1 dt\,\alpha\, |R\cdot \nabla g_a(y-t\alpha R)| \\ &\leqq \alpha \{\int dy\, |f(x-y)|\, |R| \sup_{|z|\leqq \alpha|R|} |\nabla g_a(y-z)|\}.\end{aligned}$$

Now, $f \in L^{5/2}+L^4$ and $\nabla g_a \in L^p$ for any $1 \leqq p \leqq \infty$ hence $f_a^\alpha \to f_a$ in $L^{5/2}+L^4$ as $\alpha \downarrow 0$, by using Young's inequality. $\square$

Lemma A.2. $\alpha^{-1}(f_a^\alpha - f_a) \to \partial f_a/\partial\alpha|_{\alpha=0}$ *in* $L^{5/2}+L^4$ *as* $\alpha \downarrow 0$.

Proof. We need only remark that for a $C^2(\mathbb{R})$ function h, we have

$$b^{-1}[h(a+b) - h(a)] - h'(a) = b \int_0^1 ds \int_0^s dt\, h''(a+bt),$$

for any $a, b \neq 0$. The rest of the proof proceeds as in the proof of Lemma A.1. $\square$

Lemma A.3. $U_a(\{R_i\}^\alpha)$ *(given by Eq.* (12) *with* R_1 *replaced by* $R_1+\alpha n$, $\alpha>0$, $n \in \mathbb{R}^3$*) is continuously differentiable with respect to* α *and*

$$\frac{\partial U_a(\{R_i\}^\alpha)}{\partial\alpha} = -z_1 \int [n\cdot \nabla g_a(y)]\, V_a^\alpha(y+R_1+\alpha n)\,dy. \tag{A.1}$$

Proof. We need only prove differentiability at $\alpha=0$. From (12) we get

$$\begin{aligned}&\alpha^{-1}[U_a(\{R_i\}^\alpha) - U_a(\{R_i\})] \\ &= z_1 \sum_{j=2}^k z_j \int g_a(y) g_a(x)\, \alpha^{-1}[|x-R_1-\alpha n-y+R_j|^{-1} - |x-R_1-y+R_j|^{-1}]\,dx\,dy.\end{aligned}$$

Since $|x|^{-1} \in L^{5/2}+L^4$, Lemma A.2 implies that

$$\alpha^{-1}(g_a * |x-R_1-\alpha n+R_j|^{-1} - g_a * |x-R_1+R_j|^{-1}) \to g_a * \frac{\partial}{\partial\alpha}|x-R_1-\alpha n+R_j|\Big|_{\alpha=0}$$

as $\alpha\downarrow 0$ in $L^{5/2}+L^4$. Since $g_a \in L^p$, any $1 \leqq p \leqq \infty$, and using the definition of V_a [see Eq. (10)] we have

$$\lim_{\alpha\downarrow 0} \alpha^{-1}[U_a(\{R_i\}^\alpha) - U_a(\{R_i\})] = z_1 \int g_a(y) \frac{\partial V_a^\alpha}{\partial\alpha}\Big|_{\alpha=0}(y+R_1)\,dy. \qquad (A.2)$$

[Notice that we have used $\int g_a(y)\,\partial/\partial\alpha(|y-\alpha n|^{-1})|_{\alpha=0}\,dy=0$ to obtain A.2.] Finally, (A.1) follows from (A.2) by integration by parts. □

Lemma A.4. *$f_a \to f$ in $L^{5/2}+L^4$ as $a\downarrow 0$.*

Proof. See ([10], Lemma 2.18(c)). □

Lemma A.5. *$U_a \to U$ as $a\downarrow 0$.*

Proof. We can write $U_a - U = \sum_{1\leqq i<j\leqq k} (A_{ij}+B_{ij})$ with

$$A_{ij} = \int dx\, g_a(x)\{\int g_a(y)\,|x-y+R_i-R_j|^{-1}\,dy - |x+R_i-R_j|^{-1}\}$$

and

$$B_{ij} = \int dx\, g_a(x)\,|x+R_i-R_j|^{-1} - |R_i-R_j|^{-1}.$$

Because of ([10], Lemma 2.18(e)) $\lim_{a\downarrow 0} g_a * |x+R_i-R_j|^{-1} = |x+R_i-R_j|^{-1}$ uniformly on $|x| \leqq a$ (as long as $a<|R_i-R_j|$). Hence, $A_{ij}\to 0$ as $a\downarrow 0$. Also, $B_{ij}\to 0$ as $a\downarrow 0$ because of ([10], Lemma 2.18(e)). □

Acknowledgements. I would like to thank Bradley Plohr for stimulating discussions and Elliot Lieb for useful discussions and encouragement.

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Communicated by E. Lieb

Received December 12, 1980, in revised form March 30, 1981