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LETTER TO THE EDITOR

Monotonicity of the electronic contribution to the Born–Oppenheimer energy

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Abstract. Let $E(R)$ denote the ground-state energy of a single electron and two fixed nuclei of charges z_A and z_B a distance R apart. Let $e(R) = E(R) - z_A z_B R^{-1}$ be the electronic contribution. We prove that '$e(R)$ increases as R does' in two different ways: using correlation inequalities and using the theory of log concave functions. Various extensions are described.

The Hamiltonian, H, of N infinitely heavy nucleii of charges $z_1, \ldots, z_N > 0$, at positions $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N$ and k electrons is given by

$$H = H_e + \sum_{1 \leq i < j \leq N} z_i z_j |\boldsymbol{R}_i - \boldsymbol{R}_j|^{-1}$$

$$H_e = \sum_{i=1}^{k} -\Delta_i + \sum_{i<j} |\boldsymbol{r}_i - \boldsymbol{r}_j|^{-1} - \sum_{i=1}^{k} \sum_{l=1}^{N} z_l |\boldsymbol{r}_i - \boldsymbol{R}_l|^{-1}$$

as an operator on $\mathscr{H}_{\text{phys}}$, the space of L^2 functions $\psi(\boldsymbol{r}_i, \ldots, \boldsymbol{r}_k;\ \sigma_i, \ldots, \sigma_k)$ $(\boldsymbol{r}_i \in R;\ \sigma_i = \pm 1)$, antisymmetric under the interchanges $(\boldsymbol{r}_i, \sigma_i) \leftrightarrow (\boldsymbol{r}_j, \sigma_j)$. We want to consider here the *Born–Oppenheimer* energy

$$E(\boldsymbol{R}_i) \equiv \inf \operatorname{spec}(H) = e(\boldsymbol{R}_i) + \sum_{i<j} z_i z_j |\boldsymbol{R}_i - \boldsymbol{R}_j|^{-1}$$

$$e(\boldsymbol{R}_i) = \inf \operatorname{spec}(H_e).$$

We will not concern ourselves with the validity of the Born–Oppenheimer approximation, i.e. the extent to which the Hamiltonian $\Sigma(-2M_j)^{-1}\Delta_j + E(\boldsymbol{R}_j)$ approximates the full Hamiltonian of nuclei of mass M_i and k electrons—see the preliminary report of Combes (1976) for a description of work of Aventini, Combes, Duclos, Grossman and Seiler on the subject. Rather, we will discuss the properties of $E(\boldsymbol{R}_i)$ that can be established rigorously. In this paper, we will concern ourselves with a rather special problem; a second paper (Morgan and Simon 1978) will deal with

$$\lim_{R \to \infty} E(\boldsymbol{R}_1 + \boldsymbol{R}, \ldots, \boldsymbol{R}_j + \boldsymbol{R}, \boldsymbol{R}_{j+1}, \ldots, \boldsymbol{R}_N).$$

This latter problem has been studied also by Coulson (1941), Ahlrichs (1976), Aventini

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and Seiler (1975) and Combes and Seiler (1977). We should also mention the work of Narnhofer and Thirring (1975) who establish some convexity properties of E.

Our first result is the following.

Theorem 1. Let $N = 2$, $k = 1$ and write $e(R) = e(\boldsymbol{R}_1, \boldsymbol{R}_2)$ with $R = |\boldsymbol{R}_1 - \boldsymbol{R}_2|$. Then $\mathrm{d}e/\mathrm{d}R \geqslant 0$ for $R > 0$.

More colloquially, the electronic contribution to E is attractive, at least in the case $N = 2$, $k = 1$. Thus the binding of molecules, at least in one electron molecules, involves a competition between the nuclear Coulomb repulsion and the effective attraction of H_e. This result is quite reasonable from an intuitive point of view. However, we have not been able to find a proof using 'conventional methods'; indeed, the Feynman–Hellman formula for $\mathrm{d}e/\mathrm{d}R$ is not positive by inspection. Below, we give two proofs of theorem 1.

The first proof uses correlation inequalities. These methods were developed in statistical mechanics, originally by Griffiths (1967). Their applicability to quantum systems in a Wiener path integral form was noted by Guerra *et al* (1975) who applied them to quantum field theory and certain systems with finite degrees of freedom like anharmonic oscillators. Their use in certain atomic problems not unrelated to ours has been emphasised recently by Avron *et al* (1978).

Our second proof will use ideas from the theory of log concave and symmetric decreasing functions. In particular, it will exploit the fact that a marginal integral of log concave functions is log concave. This is a theorem of Prékopa (1971); further discussion, including many applications and proofs can be found in Rinott (1973) and Brascamp and Lieb (1975, 1976). Our second proof will yield the stronger result.

Theorem 2. Let $k = 1$. Fix $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N$. Then $e(\lambda) \equiv e(\lambda\boldsymbol{R}_1, \ldots, \lambda\boldsymbol{R}_N)$ is monotonic non-decreasing as λ increases.

Unfortunately, we have very little to say about the case $k \geqslant 2$ where we believe the result is true, at least in the neutral case $k = z_1 + \ldots + z_n$ (z_i integral). In going beyond the case $k = 1$ two problems arise. The first comes from the Pauli principle. Our methods do not extend in general since they rely heavily on the existence of a positive path integral (there is one special case where we are able to extend our methods; namely to spinless fermions in one dimension which are well known to be equivalent to particles restricted to the region $r_1 < r_2 < \ldots < r_N$ with Dirichlet boundary conditions on the boundary, hence to a theory with a positive path integral). The second problem involves the electron repulsion. Again, it appears unlikely that our methods extend to $k \geqslant 2$ since they seem to exploit properties of the system that hold for arbitrary coupling constants. However, monotonicity does not hold for large values of the electron repulsion coupling constant (note that if this constant is very large, then the energy of isolated atoms is easily seen to be smaller than the energy of widely separated atoms, see Combes and Seiler 1977, Morgan and Simon 1978).

All we can report in the general k case is the following result which is elementary but often not properly appreciated (this result appeared in Narnhofer and Thirring 1975).

Theorem 3. Fix k, N, $z_1, \ldots, z_N$ positive. Then $e(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$ always takes its minimum value when all R_i are equal.

Proof. Fix $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N$ and make the z_i dependence explicit, denoting the energy simply by $e(z)$ with $z = (z_1, \ldots, z_N)$. Then $e(z)$ is jointly concave since $H_e(z)$ is linear in the z_i. This follows from the variational principle: if $z = \alpha z^{(1)} + (1 - \alpha)z^{(2)}$, $0 \leqslant \alpha \leqslant 1$, and if ψ is a wavefunction for the z problem, ψ can be used as a trial function for both the $z^{(1)}$ and $z^{(2)}$ problems. Thus

$$\alpha e(z^{(1)}) + (1 - \alpha)e(z^{(2)}) \leqslant (\psi, [\alpha H_e(z^{(1)}) + (1 - \alpha)H_e(z^{(2)})]\psi) = (\psi, H_e(z)\psi) = e(z).$$

Now let $\Sigma_1^k z_i \equiv z$. By concavity $e(z) \geqslant z^{-1}\Sigma_1^k z_i e\,(z_i = z, z_j = 0 \text{ for } j \neq i)$. But this last value of e is independent of i and is just the value of e when all the R_i are equal.

The reader should note that theorem 3 used no property of the Coulomb potential. The same theorem (and proof) would hold if the electron repulsion were replaced by any N-body potential $V(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$, and if the nuclear attraction were replaced by any single-particle potential

$$\sum_{i=1}^{N} \sum_{j=1}^{k} W(\boldsymbol{r}_i, \boldsymbol{R}_j).$$

It is not even necessary for V and W to be translation invariant.

Theorems 1 and 2, on the contrary, exploit the fact that the attractive nuclear Coulomb potential is (*a*) symmetric and (*b*) monotonic non-decreasing. The proofs we give of these theorems would hold for any one-body potential with these two properties.

Proof by correlation inequalities. This proof of theorem 1 depends on the 'easy' first Griffiths' inequality which comes from expanding an exponential in a path integral. Rather than introduce a formal path integral and then make a lattice approximation, we will merely use the Trotter product formula (which is equivalent). Since $e(R)$ is known to be real analytic (Aventini and Seiler 1975, Narnhofer and Thirring 1975) away from $R = 0$, we need only show that $e(R)$ is monotonic non-decreasing in R. Let $|\boldsymbol{x}|_\alpha = |\boldsymbol{x}|$ (resp α) if $|\boldsymbol{x}| > \alpha$ (resp $\leqslant \alpha$). Let $V_{R,\alpha} = -z_1|\boldsymbol{r}|_\alpha^{-1} - z_2|\boldsymbol{r} - (R, 0, 0)|_\alpha^{-1}$. Let ψ be a fixed positive vector and let $H_0 = -\Delta$. Then

$$-e(R) = \lim_{t\to\infty} \frac{1}{t} \ln(\psi, \exp[-t(H_0 + V_{R,0})]\psi) = \lim_{t\to\infty} \frac{1}{t} \ln\left(\lim_{\alpha\to 0} \lim_{n\to\infty} f_{n,t,\alpha}(R)\right) \qquad (1)$$

where

$$f_{n,t,\alpha}(R) = (\psi, (\exp(-tH_0/n)\exp(-tV_{R,\alpha}/n))^n\psi).$$

Clearly, it suffices, for each R, to find ψ so that

$$\frac{\partial f}{\partial R} \leqslant 0 \qquad (2)$$

for all n, t, α (actually, here we use the fact that one can show directly that the derivatives with respect to R of both sides are equal). We will take $\psi(\boldsymbol{r} = (x, y, z))$

to be a function even in x about $x = R$ for each fixed y and z. By evaluating $\partial f/\partial R$ and changing x to $R - x$, we see that (2) is implied by

$$\int \mathrm{d}x_0 \ldots \mathrm{d}x_n \,\mathrm{d}y_0 \ldots \mathrm{d}y_n \,\mathrm{d}z_0 \ldots \mathrm{d}z_n \, A_j(x_i, y_i, z_i) \geqslant 0 \tag{3}$$

with

$$A_j = h(x_j, y_j, z_j)\, \phi(x_0, y_0, z_0)\, \phi(x_n, y_n, z_n) \times \prod_{i=1}^{n} K_n(x_i - x_{i-1}, y_i - y_{i-1}, z_i - z_{i-1}) \exp[g(x_i, y_i, z_i)] \tag{4}$$

where $\phi(x, y, z) = \psi(x + R, y, z)$ is even in x and positive, K is an explicit Gaussian kernel, $h(x, y, z) = x(x^2 + y^2 + z^2)^{-3/2}$ if $|r| > \alpha$ and 0 if $|r| < \alpha$ and $-ng = tV_{R,\alpha}(x + R, y, z)$. Clearly it suffices to prove the integral in (3) is non-negative for y_i, z_i fixed. The correlation inequality we need is the following.

Lemma 1. Let $\mathscr{F}$ be the family of functions f on $(-\infty, \infty)$ of the form $f = f_{(0)} + f_{(e)}$ with $f_{(0)}$, $f_{(e)}$ positive for $x \geqslant 0$ and $f_{(e)}$(resp $f_{(0)}$) even (resp odd) in x. Then, for $f_1, \ldots, f_n \in \mathscr{F}$

$$\int f_1(x_1) \ldots f_n(x_n) \exp\left(\sum a_{ij} x_i x_j\right) \mathrm{d}x_1 \ldots \mathrm{d}x_n \geqslant 0 \tag{5}$$

if $a_{ij} \geqslant 0$.

Proof. First note that if f, $g \in \mathscr{F}$, then $fg \in \mathscr{F}$. Next note that $x \in \mathscr{F}$. Finally, note that if $f \in \mathscr{F}$, then

$$\int f \mathrm{d}x = 2 \int_0^\infty f_{(e)} \mathrm{d}x \geqslant 0.$$

Expanding the exponential in (5) and using these facts, the positivity is obvious.

Return now to (4), since $g(x, y, z) \geqslant g(-x, y, z)$ for $x > 0$, we see that

$$\exp[g(x, y, z)] = \tfrac{1}{2}\{\exp[g(x, y, z)] + \exp[g(-x, y, z)]\} + \tfrac{1}{2}\{\exp[g(x, y, z)] - \exp[g(-x, y, z)]\}$$

is in $\mathscr{F}$. Clearly, $\phi, h \in \mathscr{F}$ and if we expand

$$\exp[-a(x_i - x_{i-1})^2] = \exp(-ax_i^2) \exp(-ax_{i-1}^2) \exp(2x_i x_{i-1})$$

we see that for each y, z (4) is of the form $\Pi f_i(x_i) \exp(\Sigma a_{ij} x_i x_j)$ with $f_i \in \mathscr{F}$ and $a_{ij} \geqslant 0$. This proves (3) and therefore theorem 1.

In the above, we have actually proved the following result.

Theorem 4. Let V be a potential obeying

$$V(x, y, z) \leqslant V(-x, y, z) \qquad \text{for } x \geqslant 0 \tag{6}$$

and let Ω be the ground state for $-\Delta + V$. Let $h(x, y, z)$ be a function satisfying

$$h(x, y, z) = -h(-x, y, z) \geqslant 0$$

for all $x \geqslant 0$. Then

$$(\Omega, h\Omega) \geqslant 0.$$

(In particular,

$$\int dy\, dz \int_a^b dx |\Omega|^2 \geqslant \int dy\, dz \int_{-b}^{-a} dx |\Omega|^2$$

for all $0 < a < b$.)

From this, one concludes as in the proof of theorem 1.

Theorem 5. Let V, W obey (6). Suppose moreover, that $\partial V/\partial x \leqslant 0$ for $x \leqslant 0$ and

$$\frac{\partial W}{\partial x}(x, y, z) \geqslant \frac{\partial W}{\partial x}(-x, y, z) \quad \text{for} \quad x \geqslant 0. \tag{7}$$

Then $e(R)$, the ground-state energy of $-\Delta + W(x + R, y, z) + V(x, y, z)$ is monotonic non-decreasing in $R > 0$.

Remarks. (i) One wants $\langle \partial W/\partial x \rangle \leqslant 0$ for the potential $W(x) + V(x - R)$. To carry through the proof, we need two things: (*a*) equation (7), (*b*) $W(-x) + V(-x - R) \leqslant W(x) + V(x - R)$, $x \geqslant 0$. The first is assumed. The second is implied by $V(-x - R) \leqslant V(x - R)$, $x \geqslant 0$ and (6) for W. This in turn is implied by $\partial W/\partial x \leqslant 0, x \leqslant 0$ and (6) for V.

(ii) By comparison, the method by log concavity seems to require that V and W be even functions of x.

Proof by log concavity. We prove theorem 2 which implies theorem 1. As before, we need only show that $f_{n,t,\alpha}(\lambda)$ is monotonic decreasing in λ where

$$f_{n,t,\alpha}(\lambda) = (\psi, [\exp(-tH_0/n)\exp(-tV_\lambda/n)]^n\psi)$$

with $\psi = \exp(-r^2)$ and

$$V_\lambda(\boldsymbol{r}) = -\sum_{i=1}^{N} z_i |\boldsymbol{r} - \lambda \boldsymbol{R}_i|_\alpha^{-1}.$$

Now $\exp(z|x|_\alpha^{-1})$ is a symmetric decreasing function and therefore is an integral with positive weight of characteristic functions of balls. Thus $f_{n,t,\alpha}(\lambda)$ is an integral of functions of the form:

$$g_{n,t,\alpha}(\lambda) = \int d^3r_0 \ldots d^3r_n \psi(r_0)\psi(r_n) \prod_{i=1}^{n} K_{n,t}(r_i - r_{i-1}) \prod_{i=1}^{n}\prod_{j=1}^{N} \mathscr{X}_{a_{ij}}(r_i - \lambda \boldsymbol{R}_j) \tag{8}$$

where $\mathscr{X}_a$ is the characteristic function of the ball of radius a. The integrand in (8) is log concave jointly in $r_0, \ldots, r_n$, λ so, by the Prékopa theorem, $g(\lambda)$ is log concave in λ. Since it is also obviously even, $g(\lambda)$ is monotonic decreasing. Hence, so is f. Note $f_{n,t,\alpha}(\lambda)$ is *not* log concave since it is merely an integral of log concave functions.

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