ESD-TR-70-245

ESD ACCESSION LIST
ESTI Call No. 70899
Copy No. 1 of 1 cys.

Technical Note 1970-27

On the Theory of Localized One-Electron States in Perfect Crystals

T. A. Kaplan
P. N. Argyres

1 September 1970

Prepared under Electronic Systems Division Contract AF 19(628)-5167 by

Lincoln Laboratory
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Lexington, Massachusetts

ESD RECORD COPY
RETURN TO
SCIENTIFIC & TECHNICAL INFORMATION DIVISION
(ESTI), BUILDING 1211

AD0711372

This document has been approved for public release and sale;
its distribution is unlimited.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LINCOLN LABORATORY

ON THE THEORY OF LOCALIZED ONE-ELECTRON STATES IN PERFECT CRYSTALS

T. A. KAPLAN

Group 81

P. N. ARGYRES

Northeastern University

TECHNICAL NOTE 1970-27

1 SEPTEMBER 1970

This document has been approved for public release and sale; its distribution is unlimited.

LEXINGTON MASSACHUSETTS

The work reported in this document was performed at Lincoln Laboratory, a center for research operated by Massachusetts Institute of Technology, with the support of the Department of the Air Force under Contract AF 19(628)-5167.

This report may be reproduced to satisfy needs of U.S. Government agencies.

ABSTRACT

In a recent paper a proof was given that for a perfect crystal of hydrogen atoms, described within a certain model, the free energy corresponding to localized one-electron wave-functions was less than that corresponding to spatially extended one-electron functions. That proof, however, depended on the assumption that the summand a_ℓ appearing in the partition function for the extended solutions monotonically increases with ℓ for $\ell \geqslant 0$. The proof of this monotonicity is given here.

Accepted for the Air Force
Joseph R. Waterman, Lt. Col., USAF
Chief, Lincoln Laboratory Project Office

1. INTRODUCTION

In a recent paper[1] (to which we shall refer as I), a proof was given that for a perfect crystal of hydrogen atoms, described within a certain model, the free energy corresponding to localized one-electron functions was less than that corresponding to spatially extended one-electron functions [eq. (I3.25), i.e. eq. (3.25) of I]. These terms were defined in the framework of a new variational approximation in statistical mechanics, the thermal single-determinant approximation,[2] and under certain specified limitations on the model discussed in detail in I. This result was a central one in that paper,[1] and therefore rigor in the proof was strived for. However, the proof given (Appendix A of I) depended on the assumption (made plausible there) that the summand a_ℓ appearing in the partition function for the extended solutions [eqs. (IA.9), (IA.10)] monotonically increases with ℓ for $\ell \geq 0$. The proof of this monotonicity is presented in this report.

---

1. T. A. Kaplan and P. N. Argyres, Phys. Rev. B 1, 2457 (1970).
2. T. A. Kaplan, Bull. Am. Phys. Soc. 13, 386 (1968) and Solid State Research Report No. DDC-AD672961, Lincoln Laboratory, M.I.T. (1968:2) p. 53.

2. PROOF OF THE MONOTONICITY OF a_ℓ

For completeness we start with the definitions

$$a_\ell = \binom{N}{\frac{1}{2}N + \ell}\left(\cosh \frac{x\ell}{N}\right)^N \tag{2.1}$$

$$g_\ell \equiv \frac{a_{\ell+1}}{a_\ell} \tag{2.2}$$

ℓ is an integer. (N is used here in place of n appearing in I.) We shall prove $a_\ell \leqslant a_{\ell+1}$ for $0 \leqslant \ell \leqslant \frac{N}{2} - 1$. Thus putting

$$\frac{\ell}{N} = y \tag{2.3}$$

and

$$\ell n\ g_\ell = h(y) \tag{2.4}$$

we need to show that $h(y) \geqslant 0$ for $0 \leqslant y \leqslant \frac{1}{2} - \frac{1}{N}$, in steps of $1/N$. Equation (IA.12) gives

$$h(y) = N\ \ell n \cosh \frac{x}{N} + N\ \ell n\ (1 + \tanh \frac{x}{N} \tanh xy) + \ell n \frac{1 - 2y}{1 + 2y + \frac{1}{N}} \tag{2.5}$$

But $\ell n \cosh \frac{x}{N} \geqslant 0$, and, for $a \geqslant 0$,

$$\ell n\ (1+a) \geqslant a - \frac{a^2}{2} \tag{2.6}$$

and

$$\ln (1+a) \leqslant a \tag{2.7}$$

Thus

$$h(y) \geqslant N(\tanh \frac{x}{N} \tanh xy - \frac{1}{2} \tanh^2 \frac{x}{N}) + \ln \frac{1-2y}{1+2y} - \frac{1}{N(1+2y)} \tag{2.8}$$

But

$$\tanh a \leqslant a \quad , \quad a \geqslant 0 \tag{2.9}$$

so that (2.8) gives

$$h(y) \geqslant N \tanh \frac{x}{N} \tanh xy + \ln \frac{1-2y}{1+2y} - \frac{x^2}{2N} - \frac{1}{N(1+2y)} \tag{2.10}$$

Using (IA.27), then

$$h(y) \geqslant x \tanh xy - \ln \frac{1+2y}{1-2y} - \frac{x^2}{2N} - \frac{x^3}{3N^2} - \frac{1}{N} \tag{2.11}$$

or

$$h(y) \geqslant \gamma(y) - \mathcal{E} \equiv h_o(y) \tag{2.12}$$

where

$$\gamma(y) = x \tanh xy - \ln \frac{1+2y}{1-2y} \tag{2.13}$$

$$\mathcal{E} = \frac{x^2}{2N} + \frac{x^3}{3N^2} + \frac{1}{N} \tag{2.14}$$

The equation $\gamma(y) = 0$ arises in the thermal Hartree-Fock approximation. It is easy to see graphically (see Fig. 1) and one can show analytically that there are at most three roots $y = 0, \pm \tilde{y}$, for $|\tilde{y}| \leqslant 1/2$; also the condition for the occurrence of three roots is $x > 2$. So if we could drop ε, then we would know that $h(y) > 0$ for all y in the range 0 to $\tilde{y}$. Furthermore, $\tilde{y}$ turns out, for x as big as 100, to be extremely close to 1/2, so close that $N(\frac{1}{2} - \tilde{y}) << 1$, so we would then have completed the proof. But we have $\varepsilon \neq 0$. The functions $x \tanh xy$ and $\ell n \frac{1+2y}{1-2y}$ are shown qualitatively in Fig. 1, which is drawn for $x^2 > 4$.

Our argument is as follows. We will first show that $h(y) > 0$ for $y = \frac{1}{2} - \frac{1}{N}$, i.e. for $\ell = \frac{N}{2} - 1$ (note that for $\ell = N/2$, i.e. $y = 1/2$, $h(\frac{1}{2}) = -\infty$); that is, at the first integral step (in ℓ) towards the left from $y = 1/2$, one has passed the first crossing of $x \tanh xy$ and $\ell n \frac{1+2y}{1-2y} + \varepsilon$. It is clear (from the figure) then that $h(y)$ will remain positive as y decreases until $y = y_o$, (small and positive) is reached. We will obtain an upper bound on y_o of $2/N$. Finally we will show that g_o and g_1 are > 1 and this will conclude the proof that $a_\ell \leqslant a_{\ell+1}$ for $0 \leqslant \ell \leqslant \frac{N}{2} - 1$.

Putting $y = 1/2 - 1/N$ into (2.11), we have

$$h(\tfrac{1}{2} - \tfrac{1}{N}) \geqslant x \tanh x\ (\tfrac{1}{2} - \tfrac{1}{N}) - \ell n \frac{1 - \frac{1}{N}}{\frac{1}{N}} - \varepsilon$$

$$= x \frac{\tanh \frac{x}{2} - \tanh \frac{x}{N}}{1 - \tanh \frac{x}{2} \tanh \frac{x}{N}} - \ell n\ N(1 - \tfrac{1}{N}) - \varepsilon$$

$$\geqslant x(\tanh \tfrac{x}{2} - \tfrac{x}{N}) - \ell n\ N - \varepsilon \qquad (2.15)$$

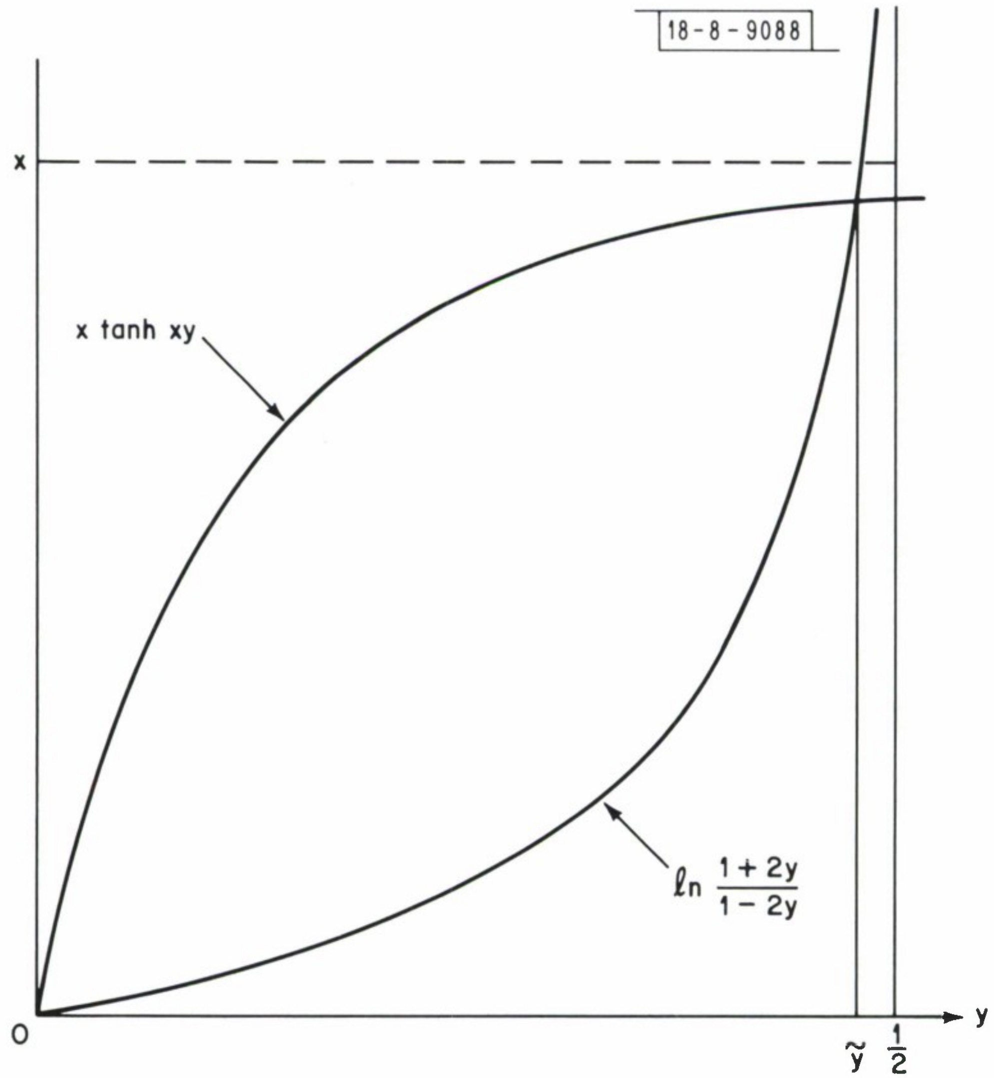

Fig. 1

For the last inequality we used $1 \geqslant \tanh \frac{x}{2} \tanh \frac{x}{N} \geqslant 0$, $\tanh \frac{x}{N} \leqslant \frac{x}{N}$. Clearly then

$$h(\tfrac{1}{2} - \tfrac{1}{N}) > 0 \text{ for } x > 200 \text{ and } N < e^{199}, \text{ but } x^2/N << 1 \tag{2.16}$$

the range discussed below Eq. (IA.17).

We now find an upper bound to the other positive root, y_o, of $h_o(y) = 0$. Put

$$\ell n \; 1{+}2y + \mathcal{E} \equiv g(y) \tag{2.17}$$

so y_o satisfies

$$x \tanh xy_o = g(y_o) \tag{2.18}$$

and is, by definition, the smallest positive root. Now $g(o) = \mathcal{E} > 0$, $\tanh xy = 0$ at $y = 0$, and both $\tanh xy$ and $g(y)$ monotonically increase with y. Hence if we replace $\tanh xy$ by $\bar{t}(y) < \tanh xy$ and replace $g(y)$ by $\bar{g}(y) > g(y)$, then

$$x\bar{t}(y_u) = \bar{g}(y_u) \tag{2.19}$$

where

$$y_u > y_o \tag{2.20}$$

(The latter may be seen very simply by graphical means.)

Using (IA.27), we will choose

$$\bar{t}(y) = xy - \frac{1}{3} x^3y^3 \tag{2.21}$$

Also

$$-\ln(1-2y) \leqslant \frac{2y}{1-2y}, \quad y \geqslant 0 \tag{2.22}$$

Proof: $f(x) \equiv \frac{x}{1-x} + \ln(1-x)$; then $f(o) = 0$

$$f'(x) = \frac{x}{(1-x)^2} > 0 \text{ for } x > 0$$

$$\therefore f(x) \geqslant 0 \text{ for } x \geqslant 0$$

So, using in addition $\ln(1+2y) \leqslant 2y$, we can choose

$$\bar{g}(y) = 4y\,\frac{1-y}{1-2y} + \varepsilon \tag{2.23}$$

Thus y_u satisfies $x\bar{t}(y) = \bar{g}(y)$, which can be written

$$(x^2-4+2\varepsilon)y = (2x^2-4)y^2 + \frac{1}{3}x^4y^3 - \frac{2}{3}x^4y^4 + \varepsilon \equiv \bar{h}(y) \tag{2.24}$$

Again: the ℓ.h.s. increases monotonically and is zero at $y = 0$, while $\bar{h}(o) = \varepsilon > 0$, so that increasing the r.h.s., $\bar{h}(y)$, will increase the smallest positive root. Clearly, for $y \leqslant 1$,

$$\bar{h}(y) \leqslant (2x^2-4)y^2 + \frac{1}{3}x^4y^2 + \varepsilon$$

so that y_u (actually bigger than the y_u satisfying (2.24)) satisfies

$$(2x^2-4+\frac{1}{3}x^4)y^2 - (x^2-4+2\varepsilon)y + \varepsilon = 0 \tag{2.25}$$

We want the root that $\rightarrow 0$ as $\varepsilon \rightarrow 0$: So

$$y_u = \frac{(x^2-4+2\varepsilon)(1 - \sqrt{1-\Gamma})}{2(2x^2-4 + \frac{1}{3}x^4)} \tag{2.26}$$

with

$$\Gamma \equiv \frac{4\varepsilon\ (\frac{1}{3}x^4 + 2x^2-4)}{(x^2-4+2\varepsilon)^2} < 1 \text{ for } x \quad 200,\ \varepsilon \sim \frac{x^2}{N} << 1 \tag{2.27}$$

Also $\sqrt{1-\Gamma} > 1-\Gamma$ for $0 < \Gamma < 1$, and $x^2-4+2\varepsilon > 0$ for our parameter range, so that

$$y_u < \frac{x^2-4+2\varepsilon}{2(\frac{1}{3}x^4 + 2x^2-4)} = \frac{2\varepsilon}{x^2}\ \frac{1}{1 - \frac{4}{x^2} + \frac{2\varepsilon}{x^2}} \equiv y_o^u \tag{2.28}$$

So

$$2 - Ny_o^u = \frac{1 - \frac{10}{x^2} + \frac{4\varepsilon}{x^2} - \frac{2x}{3N}}{1 - \frac{4}{x^2} + \frac{2\varepsilon}{x^2}} > 0 \text{ for the range of interest} \tag{2.29}$$

i.e.

$$Ny_o^u < 2 \tag{2.30}$$

which is the desired upper bound on y_o.

For g_o, we use $\cosh x > 1 + \frac{x^2}{2}$ and $\frac{x}{1+x} < \ell n\ (1+x) < x$ for $x < 1$, and find that

$$g_o = e^{N \ell n \cosh \frac{x}{N} - \ell n \, (1 + \frac{2}{N})} \geqslant e^{\frac{x^2/2N}{1 + x^2/2N^2} \left[1 - \frac{4}{x^2} \, (1 + \frac{x^2}{2N^2}) \right]}$$

(2.31)

so that $g_o > 1$ for $x \geqslant 200$ and $x^2/N << 1$.

Again

$$g_1 = (\cosh \tfrac{x}{N})^N \; (1 + \tanh^2 \tfrac{x}{N})^N \; \frac{\frac{N}{2} - 1}{\frac{N}{2} + 2}$$

$$> (\cosh \tfrac{x}{N})^N \; (1 - \tfrac{6}{N})$$

$$> e^{\frac{x^2/2N}{1 + x^2/2N^2} - \frac{6/N}{1-6/N}}$$

$$= e^{\frac{1}{N} \left[(\frac{x^2}{2} - 6) - \frac{3x^2}{N} \, (1 + \frac{1}{N}) \right] / (1 + \frac{x^2}{2N^2}) \, (1 - \frac{6}{N})}$$

$$> 1 \text{ for } x \geqslant 200, \; \frac{x^2}{N} << 1$$

(Actually, to a very good approximation,

$$g_1 \cong e^{\frac{x^2}{2N} + \frac{x^2}{N} - \frac{6}{N}} = e^{\frac{1}{N} \, (\frac{3x^2}{2} - 6)}$$ (> 1 for $x > 2$, which is the critical value in the THFA.)

DOCUMENT CONTROL DATA – R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Lincoln Laboratory, M.I.T.	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP None
3. REPORT TITLE On the Theory of Localized One-Electron States in Perfect Crystals	
4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)* Technical Note	
5. AUTHOR(S) *(Last name, first name, initial)* Kaplan, Thomas A. and Argyres, Petros N.	

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
1 September 1970	14	2

8a. CONTRACT OR GRANT NO. AF 19(628)-5167 b. PROJECT NO. 649L c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Note 1970-27 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* ESD-TR-70-245
10. AVAILABILITY/LIMITATION NOTICES This document has been approved for public release and sale; its distribution is unlimited.	
11. SUPPLEMENTARY NOTES None	12. SPONSORING MILITARY ACTIVITY Air Force Systems Command, USAF

13. ABSTRACT

In a recent paper a proof was given that for a perfect crystal of hydrogen atoms, described within a certain model, the free energy corresponding to localized one-electron wave-functions was less than that corresponding to spatially extended one-electron functions. That proof, however, depended on the assumption that the summand a_ℓ appearing in the partition function for the extended solutions monotonically increases with ℓ for $\ell \geqslant 0$. The proof of this monotonicity is given here.

14. KEY WORDS

crystal structure   hydrogen atoms   free energy