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Semiempirical Calculations of Defect Properties in LiF Crystal

I. Perfect Crystal

By

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To obtain the electronic structure of both, perfect and imperfect ionic crystals the standard calculation scheme of the INDO semiempirical method is modified in order to consider the interaction of valence electrons with ionic cores more accurately than it has been done so far. The INDO parameters are optimized to reproduce a number of experimentally observed properties of a perfect LiF crystal. The parameters derived permit to reproduce quite well the distinctive properties of free F_2^0, F_2^-, LiF molecules which is necessary for reliable calculations of the properties of intrinsic hole defects.

Для расчета электронной структуры совершенных и несовершенных ионных кристаллов предложена модифицированная расчетная схема полуэмпирического квантохимического метода ЧПДП, позволяющая более корректно, чем традиционная, учесть взаимодействие валентных электронов с остовами ионов. Параметры метода оптимизировались для воспроизведения экспериментальных характеристик совершенного кристалла LiF. Полученные параметры позволяют хорошо воспроизвести характеристики молекул F_2^0, F_2^-, LiF, что необходимо для расчета собственных дырочных дефектов.

1. Introduction

Theoretical study of imperfect ionic crystals leads to a fuller understanding of numerous processes in those crystals (impurity conduction, radiative and non-radiative recombination, carrier ionization into bands, etc.).

Estimate of the efficiency of these processes necessitates calculations of the potential energy curves for initial and final states of a defect or defect pair. For small-radius defects these potential energy curves to a good approximation are determined by the *absolute* energies of midpoints of valence and conduction bands of a perfect crystal, the interaction of a rather limited number of ions involving a defect and its environment, as well as the potential produced by the rest of the crystal. Therefore, a criterion of the reliability of defect potential energy curve calculations could be an adequate preliminary reproduction of the el ectronicstructure of a perfect crystal (in particular, of absolute energies of the bands), as well as potential energy curves of certain diatomic molecules (cf. Section 3). *Absolute* one-electron energies of defect local states (calculated at a minimum of the potential energy curves) yield e.g. asymptotics of defect wave functions whose knowledge is necessary to estimate correctly both efficiencies of the above-mentioned processes as well as defect interaction energies.

The main purpose of the present paper is a modification of a calculation scheme of the standard semiempirical method of intermediate neglect of the differential overlap (INDO) [1] (Section 2) and its parametrization (Section 3) in order to calculate correctly the properties of both perfect and imperfect crystals.

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All calculations have been done in the framework of two models of perfect and imperfect crystals: molecular cluster [2] and large unit cell [3 to 6].

The problem of how to place unique defect levels, obtained in a molecular cluster calculation in a perfect crystal gap, is also discussed.

The problems discussed in Sections 2, 3 are of primary importance for defect property calculations. Concrete calculation for a perfect LiF crystal is given in the present part of the paper whereas defect properties will be discussed in its second part.

2. Models of Perfect and Imperfect Crystals. Calculation Scheme

Adequate models for calculating the electronic structure of perfect crystals have to take into account the cyclic boundary conditions arising from the translational symmetry of a crystal. One of such suitable models retaining a quasimolecular calculation scheme is the large unit cell (LUC) model [3 to 6]. This model can, in principle, be applied also to defect calculations [7]. However, in order to obtain the properties of an isolated defect, one had better employ the rather larger unit cells, whose size becomes unreasonably large and cumbersome for such low-symmetry defects as the quasimolecular H, V_k centres studied below. On the other hand, charged defects cannot, in principle, be considered within the LUC model and hence the molecular cluster (MC) model has to be used here. A sufficiently large MC can yield rather reasonable features for the perfect ionic crystals, too [8, 9]. Further, below we employed the MC model for defect property calculations and both the MC and LUC models for a perfect LiF crystal. (A comparison of the results obtained in the framework of both these models is given in [9b].)

A concrete realization of both models requires a modification of the corresponding calculating scheme developed for molecular calculations (e.g. the INDO method in the present case). Within the MC model — unlike the LUC one — the exchange and resonance interactions between atoms are limited by the MC size. At the same time, the Coulomb interactions producing the crystal potential can be treated in the same way in *both* models [10]. Thus, the diagonal matrix element of the crystal potential for an electron occupying the μ-th AO on atom A may be written in both models as

$$V_{\mu A}^M = \sum_{B(\neq A)} \left\{ \sum_\lambda{}^B P_{\lambda\lambda} \gamma_{\mu\lambda} + V_{\mu B} \right\}, \tag{1}$$

where the first sum runs over the whole crystal, $P_{\lambda\lambda}$ are diagonal elements of the density matrix (AO populations[2])), $\gamma_{\mu\lambda} = (\mu\mu \mid \lambda\lambda)$ are two-centre Coulomb integrals calculated for valence s, p AO's (see also Section 3), whereas $V_{\mu B}$ is the interaction with the core of the B-th atom. In the standard CNDO/2 scheme it reads [1]

$$V_{\mu B} = V_{AB} = Z_B \gamma_{AB}, \tag{2}$$

where Z_B is the charge of the B-th core.[3]) In our opinion, this approximation is too rough for calculating the crystal potential. In particular, it leads to a wrong sequence of potentials in planes near the crystal surface. Results similar to ours [11] have also been obtained in a model [12] where the non-point natur of ions had been taken into account through a series expansion of the crystal potential in spherical harmonics. We employed a more correct approximation,

$$V_{\mu B} = \sum_\sigma{}^B P_{\sigma\sigma} \gamma_{\mu\sigma} - Z_B' \gamma_{\mu B}, \tag{3}$$

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[2]) Neglect of interaction with the bond charges, i.e. the terms of the $\sum^B_{\nu,\lambda} P_{\nu\lambda}(\mu\mu \mid \nu\lambda)$ type in (1) seems to be of minor importance in the ionic crystals studied.

[3]) This approximation is theoretically not well based [1], but permits to compensate for distinct errors of the zero-differential overlap approach in calculating the total energy. It allows to obtain in the CNDO/2 scheme reasonable geometry of molecules.

where σ stands for the *core* AO's of the B-th atom, Z'_B being the B-th nuclear charge, $\gamma_{\mu B} = (Z'_B \mid \mu\mu)$ are integrals of nuclear attraction.

Matrix elements within the LUC model for spin α in the unrestricted Hartree-Fock INDO method read[4]) (in standard notation [1], cf. also [4, 5])

$$F^{\alpha}_{\mu\mu} = U^{A}_{\mu\mu} + \sum_j \beta^{A}_{\mu}[S_{0\mu,j\mu} - \delta_{j0}] + \sum^{A}_{\lambda} [P_{\lambda\lambda}(\mu\mu \mid \lambda\lambda) -$$

$$- P^{\alpha}_{\lambda\lambda}(\mu\lambda \mid \mu\lambda)] + V^{M}_{\mu A}; \qquad \mu \in A , \qquad (4a)$$

$$F^{\alpha}_{\mu\nu} = (2P_{\mu\nu} - P^{\alpha}_{\mu\nu}) \, (\mu\nu \mid \mu\nu) - P^{\alpha}_{\mu\nu}(\mu\mu \mid \nu\nu); \qquad \mu, \nu \in A , \qquad (4b)$$

$$F^{\alpha}_{\mu\nu} = \tfrac{1}{6} \, (\beta^{A}_{\mu} + \beta^{B}_{\nu}) \sum_j S_{0\mu,\, j\nu} - P^{\alpha}_{\mu\nu}\tilde{\gamma}_{\mu\nu}; \qquad \mu \in A, \nu \in B . \qquad (4c)$$

Here

$$\tilde{\gamma}_{\mu\nu} = \sum_j f(\boldsymbol{R}_A - \boldsymbol{R}_B + \boldsymbol{R}_j) \, \gamma_{0\mu,\, j\nu} , \qquad (5)$$

where $\boldsymbol{R}_A(\boldsymbol{R}_B)$ are radius vectors for the A (B) atom positions within a quasi-molecule, $\boldsymbol{R}_j$ are the translation vectors of the LUC. Indices $j\mu$ stand for μ-th AO belonging to the B-th atom from the j-th elementary cell.

As is shown in [4b], the cut-off function $f(\boldsymbol{R})$ can be calculated directly for each particular Brillouin zone (BZ). However, it decreases very sharply with the distance R between atoms due to which the cut-off radius for exchange integrals can be restricted to the nearest-neighbour distance, a_0 (lattice constant 3.874 at. units) (cf. [4b, 5]). It leads also to the neglect of a similar lattice summation for one-centre Coulomb and exchange integrals in (4a) and (4b).

Lattice summation over overlap integrals $\sum_j S_{0\mu,\, j\nu}$ is rapidly convergent due to which the effective radius $R_s = 4a_0$ is quite sufficient. In calculating the crystal potential (1) the non-point nature of the lattice ions was taken into account within 48 spheres around the chosen ion. The contribution of the rest of the lattice is taken in the form of the "residual Madelung" [2, 5, 10],

$$V^{point}_{A} = \frac{MQ_A}{a_0} - \sum_{(R_j \leqq R_c)} \frac{Q_j}{R_j}, \qquad (6)$$

$Q_A = Z_A - \sum^{A}_{\lambda} P_{\lambda\lambda}$ is the effective charge of atom A, $|Q_j| = Q_A$, M the Madelung constant ($= 1.7476$ for an f.c.c. lattice).

In the perfect crystal calculations within the LUC the populations of AO's, $P_{\lambda\lambda}$, of all similar atoms from the LUC coincide. The same values obtained in each iteration were used in calculating the contribution to the matrix elements of the crystal potential (1) from atoms *outside* the LUC. In turn, when calculating both perfect and imperfect crystals within the MC model, one obtains different AO populations and charges of atoms due to their non-equivalence within a MC. (For a perfect crystal calculation it is of the order of $0.05e$.) Due to this, in calculating a perfect crystal within the MC model the populations of atoms outside the MC were taken to be equal to those obtained in each iteration for an ion with a maximum number of neighbours (e.g. central F^- in the 27 atom MC $[Li_{14}F_{13}]^+$). In doing the *defect* calculations, these populations were fixed and equal to those obtained for the above-mentioned ion in a *perfect* crystal.

Our calculations show that the matrix element of the crystal potential on *valence* AO's of cations (which are almost vacant) is 5.7 eV, i.e. considerably *less* than similar values obtained for a point-ion lattice, i.e. the Madelung potential $MQ/a_0 = 9.2$ eV

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[4]) For the MC model $j = 0$.

$(Q = 0.75e$, see [28]). This results directly from their diffusive nature $(\xi_{2s}(\mathrm{Li}^+) =$
$= 1.2r_\mathrm{B}^{-1}$, see Section 3). The corresponding orbital exponent for the anion is almost
twice greater $(\xi_{2p}(\mathrm{F}^-) \approx 2r_\mathrm{B}^{-1})$. It leads to a value 9.7 eV which is slightly exceeding
the Madelung potential. (For *core* AO's the effect of the non-point ions is negligible.)

It should be stressed that the use of the "standard" relation $V_{\mu \mathrm{B}} = Z_\mathrm{B}\gamma_\mathrm{AB}$ in [11]
instead of (2) has led to an *opposite* effect (i.e. values for valence AO's of cations ex-
ceeded those for anions). The above-described non-point effect of the crystalline field
can be important for electron centre calculations (e.g. activator centres like Tl°, In°,
etc.).

3. Parametrization Scheme and Comparison of Calculated Properties with Experimental Data

The employed parametrization scheme has been described quite recently [10]. In the
latter the direct fitting of the INDO parameters is used to obtain the experimental
properties of a perfect LiF crystal.[5]) It permits then to obtain a reliable defect struc-
ture and, in particular, defect level locations within a gap making use of *no* additional
parameters. Strictly speaking, the obtained parameters are optimum only within the
framework of a fixed calculating scheme (Section 2), a chosen basis set, and the LUC
model used.

The Slater-type AO's 2s and 2p for F^- and 2s for Li^+ are used in the basis set.
Parameters $E_\mathrm{neg}^\mathrm{A}$, ξ_μ^A, and β_μ^A are different for s and p AO's. It permits to obtain
a qualitatively right connection between the widths of the corresponding valence bands,
$\Delta E_\mathrm{s}^\mathrm{w} < \Delta E_\mathrm{p}^\mathrm{w}$, which is well known from the band structure calculations (e.g. [15, 19]).
On the other hand, the standard CNDO parametrization scheme gives an opposite
effect [4a].

The use of different parameters for s, p AO's involves a violation of the invariance
of results with respect to hybridization [1]. However, this effect is of minor importance
for the ionic compounds under study. Again, to retain result invariance with respect to
the rotation of a general coordinate system (mixing of AO's from different atoms),
two-centre Coulomb integrals $(\mu\mu \mid \lambda\lambda)$ were calculated using different ξ_μ^A values for
s, p AO's but neglecting their angular dependences, as it is done in the standard
CNDO/2 scheme [1]. It should be stressed that use of approximate formulae by Mataga
[20] or Ohno [21] along with a large cut-off radius leads first of all to a noticeable
change (a few eV) of the *absolute* energies in question.

One-centre Coulomb and exchange integrals as well as those for nuclear attraction,
$(Z'_\mathrm{B} \mid \mu\mu)$,were calculated exactly [22, 23].

The diagonal matrix elements of the interaction of an electron occupying the μ-th
valence AO on atom A with its core are of the form

$$U_{\mu\mu}^\mathrm{A} = -E_\mathrm{neg}^\mathrm{A}(\mu) - \sum_\lambda{}^\mathrm{A} \left[P_{\lambda\lambda}^{(0)}(\mu\mu \mid \lambda\lambda) - P_{\lambda\lambda}^{\alpha(0)}(\mu\lambda \mid \mu\lambda) \right] . \tag{7}$$

Here $E_\mathrm{neg}^\mathrm{A}$, $P_{\lambda\lambda}^{(0)}$ values were varied in the course of parameter optimization in order to
obtain $P_{\lambda\lambda}^{(0)}$ values coinciding with the diagonal elements of the density matrix obtained
in the self-consistent calculation. The values $U_{\mu\mu}^\mathrm{A}$ thus obtained were fixed during
defect calculations.

In a perfect crystal calculation the LUC $\mathrm{Li}_8\mathrm{F}_8$ was used which reproduces the Γ, X,
L points of the BZ, i.e. the edges of the conduction and valence bands [24]. As basic
experimental features of a crystal, which the method employed is able to reproduce

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[5]) It should be stressed that numerous band structure calculations of LiF ([2b, 4, 5, 8, 13 to 19]
and references therein) have yielded as yet properties quite divergent from the experimental data
[13].

reliably, are used: $E_p^w = 6.1$ eV [13, 25], direct band gap ≈ 14 eV [26, 27], electron affinity (the bottom of the conduction band) 0.1 eV [13], effective ionic charges $Q = \pm 0.82$ [28].

From these values one can easily calculate the midpoint of the valence band $E_p^w \approx -17$ eV (cf. [13]). Unlike the earlier parametrizations, we try to reproduce correctly the *absolute* energies, which, in our opinion, also makes parametrization and defect calculations more reliable. Thus, we make use of five experimental crystal properties to obtain six INDO parameters (ξ, β, E_{neg} for 2s Li$^+$ and 2p F$^-$). Due to a lack of experimental data for the width of the deep 2s F$^-$ valence band, we have employed the parameters ξ and β for 2s AO's close to [5]. This permits to obtain a reasonably narrow 2s valence band, i.e. narrower than the 2p band, in agreement with the band structure calculations [15, 19]. In turn, $E_{neg}^{2s}(F^-)$ has been chosen so as to obtain the experimental value -23.4 eV [5] for the separation between the top of the 2p valence band and the midpoint of the 2s band.

The relations between the method parameters and the crystal features have been discussed earlier [5, 10, 29]. However, the direct parameter fitting is complicated by the following problem.

As shown in [15, 17, 30, 31] a direct comparison of gap and midpoints of bands calculated within the Hartree-Fock method (or its simplified version as INDO is) with the experimental data is not justified. Such a comparison becomes possible only after including correlation corrections to the calculated one-electron energies [17, 30]. This leads to both a noticeable decrease of the bottom of the conduction band and an increase of the valence bands, thus reducing the gap to about 10 eV (as compared to the initial Hartree-Fock value, i.e. the difference of one-electron energies of the band edges).[6]) Correlation corrections can be separated into short-range and long-range components [17]. Based on the idea that a short-range correction (which has atomic nature and arises due to the failure of Koopmans' estimate [17] of a real ionization potential) is effectively taken into account in the course of parameter optimization, we fitted the sum of one-electron energies of band edges and corresponding long-range corrections to obtain the above given experimental LiF properties.[7]) In our opinion,

Table 1

Optimized parameters for a LiF crystal

parameters	Li$^+$		F$^-$	
	our results	[32]	our results	[32]
ξ_{2s} (r_B^{-1})	1.2	1.2	2.1	2.21
ξ_{2p} (r_B^{-1})		1.2	1.75	2.21
E_{neg}^{2s} (eV)	2.65	2.65	23.24	36.43
E_{neg}^{2p} (eV)		0.764	4.1	13.95
β (eV)	-4.5	-1.75	-10.8	-20.5

There is a misprint in our table of parameters for NaCl [10] where β-values for anion and cation should be permuted.

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[6]) Another more correct way to obtain ΔE_g is to calculate the difference of *total* energies for the ground and excited states [14].

[7]) It should be noted that these corrections are somewhat different for different models used [15, 17, 30, 31]. We employed 2.3 eV for the conduction band and 1.8 eV for the 2p valence band [30, 31].

long-range polarization corrections cannot, in principle, be taken into account through parameters and should be used for a comparison with experiment.

The derived parameters are given in Table 1. The main deviation of our parameters from those derived recently by fitting to diatomic molecules [32] consists in $E_{neg}(F^-)$. Our calculations indicate that the value $E_{neg}(F^-)$ from [32] should lead to a considerable underestimate of the width of the upper valence band. In turn, the divergence in $\xi(F^-)$'s is due to different basis sets. An inclusion of 2p AO's for Li^+ in our basis set results in an increase of E_p^w by about 1 eV which can be compensated by ξ, β changes. The distinctive properties of the LiF crystal calculated using LUC Li_8F_8 and our as well as other parametrizations are listed in Table 2. The role of the cut-off radii in the calculated properties is discussed in [4b, 5].

An adequate calculation scheme being based on error cancellation should reproduce correctly the trend of electronic structures of ions and molecules having a chemical bond different from that in compounds used for the parametrization [10]. A reasonable criterion of both suitable calculation and parametrization schemes is their ability to reproduce features of a series of defects. In the present paper as such subjects we have chosen the free molecules F_2^0, F_2^-, LiF (well studied both experimentally and ab initio), as well as F, H, V_k centres. (The last two centres are related very closely with the F_2^- quasi-molecule in a crystal.)

Our preliminary calculations of the free molecules mentioned show clearly that the consistent use of the above-described way of calculation of two-centre Coulomb interactions between atoms results in too small internuclear equilibrium distance, R_e, and too high dissociation energy, D. This indicated once more that, as a rule, parametrization and calculation schemes are suited to reproduce correctly *either* optical (one-electron) *or* spatial (connected with total energy) properties of perfect and imperfect crystals as well as molecules.

Reasonable values of R_e and D can be obtained e.g. by using the recently developed cheme [34]. However, we have successfully used another equation for the total energy

Table 2

Distinctive properties of a LiF crystal obtained in the LUC model
(energies in eV, charges in e)

property[a])	parametrization				exp. [13]	
	[1]	[33]	[32]	present paper		
$-E_m^P$	12.48	10.44		18.55	17.15[b])	(18.95)
ΔE_{2p}^W	2.02	0.37	4.9	6.0	6.1	
E_g	16.6	42.16	21.8	18.0	14.0	(18.1)
$E_{\Gamma 1c}$[c])	5.19	31.91		2.45	0.1	(2.4)
$|Q|$	0.75	0.99	0.61	0.75	0.82	[28]
R_s, (a_0)[d])	3	3	1	3		
R_e, (a_0)	3	3	1	1		

[a]) All calculated properties are given without corrections (see Section 3). To compare theory and experiment these polarization corrections were taken into account in figures given in parenthesis.

[b]) Calculated based on E_g, $E_{\Gamma 1c}$, ΔE_{2p}^W (cf. [13]).

[c]) The bottom of the conduction band.

[d]) Cut-off radii for overlap and exchange integrals.

(similar to that used in [1]),

$$E_{\text{tot}} = \frac{1}{2}\left(\bar{\varepsilon}^{\alpha} + \bar{\varepsilon}^{\beta}\right) + \frac{1}{2}\sum_{\mu\nu} H^{\text{core}}_{\mu\nu} P_{\mu\nu} + \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}}, \tag{8}$$

where $\bar{\varepsilon}^{\alpha(\beta)} = \sum_{i}^{\text{occ}} \varepsilon_i^{\alpha(\beta)}$, $\varepsilon_i^{\alpha(\beta)}$ are eigenvalues, $H^{\text{core}}_{\mu\nu}$ are elements of the core Hamiltonian [1]. In turn, the diagonal matrix elements are taken in the form

$$H^{\text{core}}_{\mu\mu} = U^A_{\mu\mu} + \sum_{B \neq A} Z_B \gamma_{AB}. \tag{9}$$

Thus, when calculating the total energy, we combined both the $V_{AB} = Z_B \gamma_{AB}$ approximate relation employed in the CNDO/2 scheme and the more refined procedures (1), (3) for calculating $\varepsilon_i^{\alpha(\beta)}$ and $P_{\mu\lambda}$. It permits *without* additional parameters (unlike [34]) to reproduce potential energy curves for LiF, F_2^- molecules in good agreement with the ab initio calculations [35], see Table 3.

Table 3
Properties of diatomic molecules obtained using equation (7) and parameters from Table 2

species	D (eV)	R_e (at. units)
F_2^0	6.3 (1.65)*)	3.2 (2.7)*)
F_2^-	1.67 (1.66)*)	3.6 (3.6)*)
LiF	4.20 (1.97)**)	2.85 (2.85)**)

*) Ab initio calculation [35].
**) Experimental data [37].

The optical absorption energies for a F_2^- molecule are also close to the experimental values. In Table 4 the eigenvalues for a F_2^0 molecule are listed, one can see that the agreement with the ab initio calculation is good. It is encouraging and argues for the ability of our scheme to obtain reliably *both* one-electron and bond properties of objects

Table 4
Energies of MO's for a F_2^0 molecule obtained using parameters from Table 2

MO	energy (eV)	ab initio [36]
$1\pi_g$	17.35 (16.75)*)	18.04 (16.73)*)
$3\sigma_g$	20.50	20.30
$1\pi_u$	21.51	21.92
$2\sigma_u$	40.68	37.34
$2\sigma_g$	43.35	47.79

*) Ionization potential calculated using Δ_{SCF} method.

with chemical bonds quite different from an infinite ionic crystal used in the parametrization.

There also exists the known problem of placing the one-electron defect levels with respect to the band edges of the perfect crystal [38 to 44]. The absolute energies of the defect levels depend on the size, the shape, and the total charge of the MC used. It necessitates some procedure by which the results of MC calculations could be extrapolated to the infinite growth of its size. Our investigations demonstrated clearly that, to a good approximation, a shift of one-electron energies is due to a change of the Coulomb interactions of defect electrons with the surrounding ions of the MC whose effective charges are changing with the enlargement of MC. (The spin density of unpaired electrons of the defect should be subtracted from these charges.) The change of effective charges as compared with the LUC results is $\lesssim 0.03e$, while the corresponding Coulomb shift is ≈ 0.5 eV. This procedure can be used either directly in the course of calculating the electronic structure of defects (when it appears in fact as the self-consistence in the diagonal elements of the spin density matrix) or calculating these corrections post factum. For well-localized defects both ways yield close results.[8])

Having considered all details and modifications of the INDO calculation and parametrization schemes we shall turn in the second part of the paper to the defect calculations.

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[8]) The calculation of charged defects needs also a correction of the long-range lattice polarization [9b]. We have neglected such a correction for the V_K centre (considered in Part II) because of its smallness (≈ 0.5 eV [40]) (see, however, [9]).

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