PHYSICAL REVIEW A VOLUME 17, NUMBER 1 JANUARY 1978

# Exchange perturbation theory. II. Eisenschitz-London type*

E. E. Polymeropoulos[†‡] and William H. Adams
School of Chemistry, Rutgers University, New Brunswick, New Jersey 08903
(Received 22 March 1977)

An exchange perturbation theory is developed which is identical through first order in the primitive function $G$ with the Eisenschitz-London (EL) theory. It is shown that in higher orders, $G$ is different from the EL primitive function and from the primitive functions of related theories. The function $G$ is least distorted from the zeroth-order function $F^0$, a product of functions for the subsystems when the interactions have been set equal to zero. The potential which distorts $F^0$ into $G$ is more thoroughly screened than in any other theory we have examined. We argue that this EL-type theory should be used when the unscreened interactions are strong.

## I. INTRODUCTION

In this paper, we specialize the general equations of paper I[1] to the primitive function $G$ which has the property specified by Eq. (I.3) [we use (I.3) as shorthand for Eq. (3) of paper I], namely, that from $G$ one can obtain by symmetry projection one and only one eigenfunction of $\hat{H}$. This is just the property that the Eisenschitz-London (EL) EPT[2] has. This is one reason why we refer to the perturbation theory developed herein as the EL LW EPT. A second reason is that the first-order $G$ is identical to the EL first-order primitive function.

In I we showed that by defining $G$ to be least distorted from $F^0$ in the sense of (I.2) and to have the property (I.3), a perturbation theory could be developed on the basis of the screened potential of interaction $\hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q}$ with $\hat{Q}$ defined by (I.5b) or, equivalently, by (I.5b′). We argued in I that with $\hat{Q}$ defined by (I.5b) one had maximum screening of $\hat{V}_1$ by $\hat{Q}\hat{V}_1\hat{Q}$, i.e., that the resultant $\hat{V}_1 - \hat{Q}\hat{V}_1\hat{Q}$ is the weakest perturbation that is consistent with the solution of (I.11) satisfying (I.3) in the limit of $\lambda = 1$. This EL-type primitive function must therefore be the ideal function to calculate by perturbation methods, for the weaker the perturbation, the more likely it should be that the expansion will converge.

There is, unfortunately, a possible disadvantage to making the perturbation as weak as possible. The disadvantage is that the resultant expansion could be more slowly convergent than one based on a perturbation in which $\hat{V}_1$ is less effectively screened. If one cuts off the expansion of $G$ with the first-order term, it may be that the EL LW theory will be less accurate than one based on a stronger screened interaction potential.

A characteristic of the EL EPT and of those EPT's which give the same first-order function,[3-6] is that they significantly underestimate the interaction energy in $H_2^+$ and $H_2$ at large nuclear separations.[7-9] A related result is found in calculations on solvable models.[10-12] These results are consistent with the argument in the preceding paragraph.

In some discussions of the results of applying EL-type EPT's to $H_2^+$ and $H_2$, it has been said that they give the wrong asymptotic behavior for both the primitive function and the energy.[7-9] We disagree with this statement for two reasons. Firstly, there is no reason why two different EPT's should have the same asymptotic behavior in corresponding orders. One can be more accurate in $n$th order than the other, but as long as both can be assumed to be convergent, the one that is less rapidly convergent cannot be called wrong. Secondly, the correct asymptotic behavior in first order is identified as that found using the symmetry-projected polarization EPT.[7-9] In I we describe the well-known inadequacies of this EPT. It is hardly appropriate to use it as a standard to which other theories should be compared.

In Sec. II we compare the EL LW equation with the equations which have served as the starting points for the development of previous EL-type EPT's and show that they are different. Thus, the EL LW EPT must be different from those previously proposed.

In Sec. III we present the perturbation equation, and in Sec. IV the energy expansions. It is shown in Sec. III that in first order the EL LW is identical to the EL first-order function, but that the second-order functions must be different.

## II. COMPARISON TO OTHER EXCHANGE PERTURBATION THEORIES

In I we did not show that the general perturbation equations we derived were different from all that had previously been proposed. We assumed that because we had added something new to the development of EPT's, the least distortion requirement, the LW EPT's would be different. We now show that the EL LW EPT must differ from the other EL-type theories.

The primitive function $G$ of the EL LW EPT satisfies Eq. (I.16) with $\hat{Q}(\lambda)$ defined by (I.5b), explicitly,

$$\{\hat{H}_1 + \lambda \hat{e}^{\mu}_{ii}[1 - M(\lambda)\,|G(\lambda)\rangle\langle G(\lambda)\,|\,\hat{e}^{\mu}_{ii}]\hat{V}_1\}G(\lambda) = \epsilon(\lambda)G(\lambda)\,. \tag{1}$$

This expression may be rewritten with the aid of (I.25) and (I.29):

$$\{\hat{H}_1 + \hat{e}^{\mu}_{ii}[\lambda\hat{V}_1 - {}^{\text{II}}E^{\mu}(\lambda)]\}\,G(\lambda) = \epsilon(\lambda)(1 - \hat{e}^{\mu}_{ii})G(\lambda)\,. \tag{2}$$

If the primitive function of any other EL-type theory satisfies an equation identical with (2), the EL LW EPT could be identical with it. Whether or not it is, depends also on what is chosen as the perturbation.

The primitive function $\chi(\lambda)$ of the van der Avoird[5] and Hirschfelder[6] EPT's satisfies Hirschfelder's Eq. (3),[6] which, in our notation and with the $\epsilon^0$ terms moved to the right, is

$$\{\hat{H}_1 + e^{\mu}_{ii}[\lambda\hat{V}_1 - E(\lambda)]\}\,\chi(\lambda) = \epsilon^0(1 - e^{\mu}_{ii})\chi(\lambda)\,. \tag{3}$$

Even if one chooses to define $E(\lambda)$ by (I.25) with $\chi(\lambda)$ substituted for $G(\lambda)$, $\chi(\lambda)$ and $G(\lambda)$ will be different because the right side of Eq. (2) is not identical to that of (3). The EL LW EPT does belong, however, to the general class of theories recognized by Hirschfelder in his Eq. (2).[6]

The primitive function $\chi$ of the Murrell-Shaw[3] Musher-Amos[4] (MSMA) EPT can be seen to be different from $G(\lambda)$ by referring to the definition of $\chi(\lambda)$ given by Amos[13] in his Eq. (17). In our notation the definition is

$$\chi = \Psi^{\mu}_{\alpha i} + (1 - \hat{e}^{\mu}_{ii})F^0\,. \tag{4}$$

If the same normalization is adopted for $G$, then it follows from (I.3) that

$$G = \Psi^{\mu}_{\alpha i} + (1 - \hat{e}^{\mu}_{ii})\Phi \tag{5}$$

and from (I.2) that $\Phi$ must make $\epsilon$ an extremum as defined by (I.2). In general, substituting $F^0$ for $\Phi$ in (I.2) does not make $\epsilon$ an extremum. We conclude that the EL LW is not identical to the MSMA primitive function.

The perturbation theory developed by Peierls[14] has been shown by Mann[15] to belong to the general class of theories considered by Hirschfelder.[6] Mann's Eq. (7) in our notation is

$$(\hat{H}_1 + \hat{V}_1 - E)\Phi = (1 - \hat{e}^{\mu}_{ii})(1 - \hat{\Theta}\,\hat{e}^{\mu}_{ii})(\hat{V}_1 - E + \epsilon^0)\Phi\,, \tag{6}$$

where $\hat{\Theta}$ is an arbitrary operator. One can see that if $\hat{\Theta}$ were the null operator, (6) would be identical to (3), as was remarked by Mann. Mann has not considered a choice of $\hat{\Theta}$ which would make (6) identical to (2).

We have purposely left for last the comparison of the EL LW EPT to the original EL theory.[2] This is because it is not clear to us what equation the EL primitive function, summed to infinite order, should satisfy. On the basis of Eisenschitz and London's Eqs. (47)–(51), we infer that it would satisfy Eq. (3) and, therefore, that their primitive function is not identical to ours.

We have compared the EL LW to the primitive functions of all of the EPT's which give in first order the EL first-order function which differs from it only by an orthogonality condition. Since the primitive functions of these theories satisfy equations which are not identical to those satisfied by the EL LW, we conclude that the EL LW EPT cannot be identical to any of these theories.

## III. PERTURBATION EQUATIONS FOR $G$ and $\epsilon$

The equations for the perturbation determination of $G$ and $\epsilon$ are derived from the equations of I by introducing explicitly the definition of $\hat{Q}$ by (I.5b). The resultant equations are simpler than the general equations and in a form that may be more easily programmed. Note that in deriving the perturbation equations, we imposed the intermediate normalization condition on $G$, i.e., $\langle F^0|G^{(n)}\rangle = 0$ for $n \geq 1$.

From the equations for $G^{(n)}$ and $\epsilon^{(n)}$ it will be apparent that they depend on the symmetry state $\mu i$ and on $F^0$ being either a ground- or excited-state eigenfunction of $\text{H}_1$. Because it is apparent, we have not added the labels $\mu$, $i$, etc., to the $G^{(n)}$, $\epsilon^{(n)}$, $\hat{Q}^{(n)}$ and various quantities used in the derivation.

The $\hat{Q}(\lambda)$ used in the EL LW EPT is

$$\hat{Q}(\lambda) = M(\lambda)\,\hat{e}^{\mu}_{ii}\,|G(\lambda)\rangle\langle G(\lambda)\,|\hat{e}^{\mu}_{ii} + 1 - \hat{e}^{\mu}_{ii}. \tag{7}$$

We expand $\hat{Q}(\lambda)$ in a power series in $\lambda$ as indicated in Eq. (I.14). We do this by first expanding $M(\lambda)$ in the form

$$M(\lambda) = M^{(0)}\{1 + \lambda M^{(1)} + \lambda^2 M^{(2)} + \cdots\}\,, \tag{8}$$

where

$$M^{(0)} = \langle F^0|\hat{e}^{\mu}_{ii}\,|F^0\rangle^{-1}\,, \tag{9}$$

$$M^{(1)} = -2\,M^{(0)}\text{Re}\langle F^0|\hat{e}^{\mu}_{ii}\,|G^{(1)}\rangle\,, \tag{10}$$

$$M^{(2)} = M^{(1)2} - M^{(0)}(\langle G^{(1)}\,|\hat{e}^{\mu}_{ii}\,|G^{(1)}\rangle + 2\text{Re}\langle F^0|\hat{e}^{\mu}_{ii}\,|G^{(2)}\rangle)\,. \tag{11}$$

The expressions for the $\hat{Q}^{(n)}$ are given in terms of the $M^{(n)}$ and operators $\hat{P}^{(n)}$, defined below.

$$\hat{Q}^{(0)} = 1 - \hat{e}^{\mu}_{ii} + \hat{P}^{(0)} , \tag{12a}$$

$$\hat{P}^{(0)} = M^{(0)} \hat{e}^{\mu}_{ii} | F^0 \rangle \langle F^0 | \hat{e}^{\mu}_{ii} , \tag{12b}$$

$$\hat{Q}^{(1)} = M^{(1)} \hat{P}^{(0)} + \hat{P}^{(1)} , \tag{13a}$$

$$\hat{P}^{(1)} = M^{(0)} \hat{e}^{\mu}_{ii} ( |F^0\rangle\langle G^{(1)} | + |G^{(1)}\rangle\langle F^0 | ) \hat{e}^{\mu}_{ii} , \tag{13b}$$

$$\hat{Q}^{(2)} = M^{(2)} \hat{P}^{(0)} + M^{(1)} \hat{P}^{(1)} + \hat{P}^{(2)} , \tag{14a}$$

$$\hat{P}^{(2)} = M^{(0)} \hat{e}^{\mu}_{ii} ( |G^{(1)}\rangle\langle G^{(1)} | + |F^0\rangle\langle G^{(2)}| + |G^{(2)}\rangle\langle F^0 | ) \hat{e}^{\mu}_{ii} . \tag{14b}$$

These expressions are substituted into Eqs. (I.18)–(I.22).

The specialization of the equations of I to the EL LW EPT is straightforward through the first order:

$$\hat{H}_1 F^0 = \epsilon^0 F^0 , \tag{15}$$

$$\epsilon^{(1)} = 0 , \tag{16a}$$

$$E^{\mu(1)}_{\mathrm{HL}} = M^{(0)} \langle F^0 | \hat{V}_1 \hat{e}^{\mu}_{ii} | F^0 \rangle . \tag{16b}$$

The quantity $E^{\mu(1)}_{\mathrm{HL}}$ will be discussed further in Sec. IV. It is straightforward to derive

$$(\hat{H}_1 - \epsilon^0) G^{(1)} = - \hat{e}^{\mu}_{ii} (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) F^0 , \tag{16c}$$

but to show that

$$\epsilon^{(2)} = - \langle G^{(1)} | \hat{e}^{\mu}_{ii} (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) | F^0 \rangle \tag{17a}$$

$$= - \langle G^{(1)} | (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) \hat{e}^{\mu}_{ii} | F^0 \rangle \tag{17b}$$

requires the aid of (16c) and the commutator equality

$$[\hat{V}_1, \hat{e}^{\mu}_{ii}] = [\hat{e}^{\mu}_{ii}, \hat{H}_1] . \tag{18}$$

A third expression for $\epsilon^{(2)}$ can be derived from

$$\epsilon = \langle G | \hat{H}_1 | G \rangle / \langle G | G \rangle , \tag{19}$$

$$\epsilon^{(2)} = \langle G^{(1)} | \hat{H}_1 - \epsilon^0 | G^{(1)} \rangle . \tag{17c}$$

It is clear from this that $\epsilon^{(2)}$ is real. The first two expressions for $\epsilon^{(2)}$ are used in the derivation of

$$(\hat{H}_1 - \epsilon^0) G^{(2)} = \epsilon^{(2)} (1 - 2 M^{(0)} \hat{e}^{\mu}_{ii}) F^0 - \hat{e}^{\mu}_{ii} (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) G^{(1)} . \tag{17d}$$

The expression for $\epsilon^{(3)}$ derived from (19) is

$$\epsilon^{(3)} = 2 \mathrm{Re} \langle G^{(1)} | \hat{H}_1 - \epsilon^0 | G^{(2)} \rangle . \tag{20a}$$

Use (17d) in (20a) to derive

$$\epsilon^{(3)} = 2 \epsilon^{(2)} M^{(1)} - 2 \langle G^{(1)} | \hat{e}^{\mu}_{ii} (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) | G^{(1)} \rangle . \tag{20b}$$

That $\langle G^{(1)} | \hat{e}^{\mu}_{ii} (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) | G^{(1)} \rangle$ is real follows from (9), (17c) and (20a). If one substitutes (16c) in (20a), one obtains the alternative expression

$$\epsilon^{(3)} = -2 \mathrm{Re} \langle F^0 | (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) e^{\mu}_{ii} | G^{(2)} \rangle . \tag{20c}$$

Note that once $G^{(1)}$ has been determined, $\epsilon^{(3)}$ can be calculated. The highest-order equation we solve in our numerical studies is

$$(H_1 - \epsilon^0) G^{(3)} = \{ \epsilon^{(3)} - M^{(0)} [ \tfrac{3}{2} M^{(0)} \epsilon^{(3)} + (1 - M^{(0)} + M^{(0)} M^{(1)}) \epsilon^{(2)} ] \hat{e}^{\mu}_{ii} \} F^0 + \epsilon^{(2)} (1 - 2 M^{(0)} \hat{e}^{\mu}_{ii}) G^{(1)} - \hat{e}^{\mu}_{ii} (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) G^{(2)} . \tag{20d}$$

Use (19) and (20c) to derive

$$\epsilon^{(4)} = \epsilon^{(2)} [ \langle G^{(1)} | G^{(1)} \rangle - 3 M^{(0)} \langle G^{(1)} | \hat{e}^{\mu}_{ii} | G^{(1)} \rangle + ( \tfrac{3}{2} M^{(0)\,-1} - 1 ) M^{(1)} + M^{(2)} ] + \tfrac{3}{2} \epsilon^{(3)} M^{(1)} - 3 \mathrm{Re} \langle G^{(1)} | \hat{e}^{\mu}_{ii} (\hat{V}_1 - E^{\mu(1)}_{\mathrm{HL}}) | G^{(2)} \rangle . \tag{21}$$

This is the highest-order $\epsilon^{(n)}$ evaluated in our calculations.

It should be noted that Eq. (16c) is the first-order equation of the EL EPT.[2,6] Since the EL first-order function is orthogonal to $F^0$ as is $G^{(1)}$, it must be identical to $G^{(1)}$. If the first-order function of the Murrell-Shaw Musher-Amos (MSMA) EPT[3,4] is required to be orthogonal to $F^0$, it is also identical to $G^{(1)}$. The first-order function of the van der Avoird–Hirschfelder (VAH)[5,6] theory satisfies (16c), but is defined to be orthogonal to $\hat{e}^{\mu}_{ii} F^0$ rather than $F^0$. To this extent it differs from $G^{(1)}$. Thus, *through first order* in the primitive function, the EL LW theory adds to the existing EPT's only the insight that the primitive function is least distorted from $F^0$ through first order.

The EL LW EPT function differs in second order from the functions of the previously proposed theories even if the same normalization is imposed. In our notation, the second-order MSMA equation, as described by Amos,[13] is

$$(\hat{H}_1 - \hat{E}^0) \chi^{(2)} = (E^{(1)}_{\mathrm{HL}} - \hat{V}_1) \chi^{(1)} + E^{(2)} F^0 .$$

A major difference between this equation and (17d), is that $\hat{e}^{\mu}_{ii}$ appears in (17d). Similarly, the VAH second-order equation[6] differs from (17d) due to the term $\epsilon^{(2)} F^0$ which appears in the latter. Thus, even if one were to impose the intermediate normalization condition, the one we have adopted, on the VAH second-order function, it would differ from $G^{(2)}$. We conclude that only the EL LW function is least distorted from $F^0$ to all orders in the perturbation.

## IV. ENERGY EXPANSIONS

We derive the coefficients of $\lambda^n$ in the power-series expansions of the energy expressions defined in I, Sec. IV. The expansions are given only through third order and primarily to show that three of the $E^{\mu}(\lambda)$'s are inequivalent. For the reasons given in Sec. IV of I, we doubt that these expansions are otherwise useful, but we have tested them in our calculations.

### A. Expansion of ${}^{\mathrm{I}}E^{\mu}(\lambda)$

From the definition (I.28) and from (15) we find

$$ {}^{\mathrm{I}}E^{\mu}(\lambda)=\epsilon^0+\lambda\langle F^0|\hat{V}_1\hat{e}^{\mu}_{ii}|G(\lambda)\rangle\langle F^0|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle^{-1}. \quad (22)$$

Expansion of this equation in powers of $\lambda$ gives

$$ {}^{\mathrm{I}}E^{\mu(0)}=\epsilon^0, \quad (23)$$

$$ {}^{\mathrm{I}}E^{\mu(1)}=\langle F^0|\hat{V}_1\hat{e}^{\mu}_{ii}|F^0\rangle M^{(0)}, \quad (24)$$

$$ {}^{\mathrm{I}}E^{\mu(2)}=\langle F^0|(\hat{V}_1-{}^{\mathrm{I}}E^{\mu(1)})\hat{e}^{\mu}_{ii}|G^{(1)}\rangle M^{(0)}, \quad (25)$$

$$ {}^{\mathrm{I}}E^{\mu(3)}=\langle F^0|(\hat{V}_1-{}^{\mathrm{I}}E^{\mu(1)})\hat{e}^{\mu}_{ii}|G^{(2)}\rangle M^{(0)} - {}^{\mathrm{I}}E^{\mu(2)}\langle F^0|\hat{e}^{\mu}_{ii}|G^{(1)}\rangle M^{(0)}. \quad (26)$$

It is possible to relate these expressions to some of the quantities defined in Sec. III and in I.

It was shown by Hirschfelder[6] that

$$\langle F^0|\hat{V}_1\hat{e}^{\mu}_{ii}|F^0\rangle=\langle F^0|\hat{e}^{\mu}_{ii}\hat{V}_1|F^0\rangle. \quad (27)$$

Thus, from (24) and (I.26c) we get

$$ {}^{\mathrm{I}}E^{\mu(1)}=E^{\mu(1)}_{\mathrm{HL}}. \quad (28)$$

This is one of the constraints normally imposed in deriving an EPT.

If one compares (25) to (17a)–(17c), and recalls (28), one concludes that

$$ {}^{\mathrm{I}}E^{\mu(2)}=-\epsilon^{(2)}M^{(0)}. \quad (29)$$

Furthermore, $\epsilon^{(2)}$ is real by (17c) and $M^{(0)}$ by (9), so that $E^{\mu(2)}$ must also be real.

Compare (26) to (20c) and use (10) to see that

$$\mathrm{Re}({}^{\mathrm{I}}E^{\mu(3)})=-\tfrac{1}{2}(\epsilon^{(3)}+\epsilon^{(2)}M^{(1)})M^{(0)}. \quad (30)$$

If the functions $G^{(n)}$ are real, then ${}^{\mathrm{I}}E^{\mu(3)}$ is fully determined by (30). Note that $\mathrm{Re}({}^{\mathrm{I}}E^{\mu(3)})$ may be calculated even if only $F^0$ and $G^{(1)}$ are known since these functions determine $\epsilon^{(3)}$ by (20b).

The second-order energy ${}^{\mathrm{I}}E^{\mu(2)}$ is identical to the EL second-order energy.

### B. Expansion of ${}^{\mathrm{II}}E^{\mu}(\lambda)$

The definition of ${}^{\mathrm{II}}E^{\mu}(\lambda)$ by Eq. (I.29) combined with (1) gives

$$ {}^{\mathrm{II}}E^{\mu}(\lambda)=\epsilon(\lambda)+\lambda\langle G(\lambda)|\hat{e}^{\mu}_{ii}\hat{V}_1|G(\lambda)\rangle \times\langle G(\lambda)|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle^{-1}. \quad (31)$$

The expansion of ${}^{\mathrm{II}}E^{\mu}(\lambda)$ in powers of $\lambda$ is straightforward. We find

$$ {}^{\mathrm{II}}E^{\mu(0)}=\epsilon^0, \quad (32)$$

$$ {}^{\mathrm{II}}E^{\mu(1)}=E^{\mu(1)}_{\mathrm{HL}}, \quad (33)$$

$$ {}^{\mathrm{II}}E^{\mu(2)}=\epsilon^{(2)}+{}^{\mathrm{II}}D^{\mu(2)}, \quad (34a)$$

$$ {}^{\mathrm{II}}D^{\mu(2)}=[\langle F^0|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})|G^{(1)}\rangle + \langle G^{(1)}|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})|F^0\rangle]M^{(0)}, \quad (34b)$$

$$ {}^{\mathrm{II}}E^{\mu(3)}=\epsilon^{(3)}+[\langle F^0|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})|G^{(2)}\rangle + \langle G^{(2)}|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})|F^0\rangle + \langle G^{(1)}|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})|G^{(1)}\rangle]M^{(0)} + M^{(1)}\,{}^{\mathrm{II}}D^{\mu(2)}. \quad (35)$$

Note that the zeroth- and first-order energies satisfy the conditions customarily imposed on $E^{\mu}(\lambda)$ in EPT, i.e., Eqs. (I.26a) and (I.26c). It is possible to simplify the expressions for ${}^{\mathrm{II}}E^{\mu(2)}$ and ${}^{\mathrm{II}}E^{\mu(3)}$ and show that they are really quite different from ${}^{\mathrm{I}}E^{\mu(2)}$ and ${}^{\mathrm{I}}E^{\mu(3)}$, respectively.

Compare Eq. (34b) to (17a) and (17b) and recall that $\epsilon^{(2)}$ is real to see that ${}^{\mathrm{II}}D^{\mu(2)}=-2\epsilon^{(2)}M^{(0)}$. It then follows from (34a) that

$$ {}^{\mathrm{II}}E^{\mu(2)}=\epsilon^{(2)}(1-2M^{(0)}). \quad (36)$$

One has only to compare this with (29) to see that in general ${}^{\mathrm{II}}E^{\mu(2)}\neq{}^{\mathrm{I}}E^{\mu(2)}$.

In order to simplify ${}^{\mathrm{II}}E^{\mu(3)}$, we must first relate $\langle F^0|\hat{e}^{\mu}_{ii}\hat{V}_1|G^{(2)}\rangle$ and $\langle G^{(2)}|\hat{e}^{\mu}_{ii}\hat{V}_1|F^0\rangle$. From the commutation of $\hat{H}_1+\hat{V}_1$ and $\hat{e}^{\mu}_{ii}$ we find with the aid of (17a)–(17d)

$$\langle F^0|[\hat{V}_1,\hat{e}^{\mu}_{ii}]|G^{(2)}\rangle=\langle F^0|\hat{e}^{\mu}_{ii}(\hat{H}_1-\epsilon^0)|G^{(2)}\rangle =\epsilon^{(2)}(M^{(0)\,-1}-1).$$

Substitution of the complex conjugate of this in (35) gives

$$ {}^{\mathrm{II}}E^{\mu(3)}=\epsilon^{(3)}+[2\,\mathrm{Re}\langle F^0|(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})\hat{e}^{\mu}_{ii}|G^{(2)}\rangle + \epsilon^{(2)}(1-M^{(0)\,-1}) + \langle G^{(1)}|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})|G^{(1)}\rangle]M^{(0)} + M^{(1)}\,{}^{\mathrm{II}}D^{\mu(2)}$$

The final expression is obtained by substituting Eqs. (10), (20b), (20c), and the simplified form of $D^{\mu(2)}$:

$$ {}^{\mathrm{II}}E^{\mu(3)}=\epsilon^{(3)}(1-\tfrac{3}{2}M^{(0)}) + \epsilon^{(2)}(M^{(0)}-M^{(0)}M^{(1)}-1). \quad (37)$$

It is clear from this equation and (30) that ${}^{\mathrm{II}}E^{\mu(3)}\neq{}^{\mathrm{I}}E^{\mu(3)}$. Note that one needs only $F^0$ and $G^{(1)}$ to evaluate ${}^{\mathrm{II}}E^{\mu(3)}$.

### C. Expansion of ${}^{\mathrm{III}}E^{\mu}(\lambda)$

From the definition of ${}^{\mathrm{III}}E^{\mu}(\lambda)$ in (I.30) we see with the aid of (1) that

$$ {}^{\mathrm{III}}E^{\mu}(\lambda)=\epsilon(\lambda)+\lambda\langle G(\lambda)|\hat{V}_1\hat{e}^{\mu}_{ii}|G(\lambda)\rangle \times\langle G(\lambda)|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle^{-1}. \quad (38)$$

We see from (31) that ${}^{\mathrm{III}}E^{\mu}(\lambda)$ is the complex conjugate of ${}^{\mathrm{II}}E^{\mu}(\lambda)$. However, it follows from (1) and the commutation of $\hat{H}_1+\hat{V}_1$ with $\hat{e}^{\mu}_{ii}$ that ${}^{\mathrm{II}}E^{\mu}(\lambda)$ is always real, so that ${}^{\mathrm{III}}E^{\mu}(\lambda)={}^{\mathrm{II}}E^{\mu}(\lambda)$.

### D. Expansion of ${}^{\mathrm{IV}}E^{\mu}(\lambda)$

Although in the limit $\lambda=1$, ${}^{\mathrm{IV}}E^{\mu}(\lambda)$ is identical to ${}^{\mathrm{II}}E^{\mu}(\lambda)$, for $\lambda$ less than 1 it is a quite different function. It is the one energy expansion that we consider in which the zeroth energy is not $\epsilon^0$ and the first-order energy is not $E^{\mu(1)}_{\mathrm{HL}}$.

It follows from the definition of ${}^{\mathrm{IV}}E^{\mu}(\lambda)$ in (I.31), Eq. (1), and the commutation of $\hat{H}_1+\hat{V}_1$ with $\hat{e}^{\mu}_{ii}$ that

$$
\begin{aligned}
{}^{\mathrm{IV}}E^{\mu}(\lambda)=\epsilon(\lambda)+[&\langle G(\lambda)|(1-\hat{e}^{\mu}_{ii})\hat{V}_1\hat{e}^{\mu}_{ii}|G(\lambda)\rangle \\
&+\lambda\langle G(\lambda)|\hat{e}^{\mu}_{ii}\hat{V}_1\hat{e}^{\mu}_{ii}|G(\lambda)\rangle] \\
&\times\langle G(\lambda)|\hat{e}^{\mu}_{ii}|G(\lambda)\rangle^{-1}.
\end{aligned}
\tag{39}
$$

Note that the first matrix element involving $\hat{V}_1$ is not multiplied by $\lambda$ and that therefore it can contribute to ${}^{\mathrm{IV}}E^{\mu(0)}$. We set

$$
{}^{\mathrm{IV}}E^{\mu(n)}=\epsilon^{(n)}+{}^{\mathrm{IV}}D^{\mu(n)}
\tag{40}
$$

and obtain from the power-series expansion of (39) with the aid of various relationships we have already derived,

$$
{}^{\mathrm{IV}}D^{\mu(0)}=E^{\mu(1)}_{\mathrm{HL}}-\langle F^0|\hat{e}^{\mu}_{ii}\hat{V}_1\hat{e}^{\mu}_{ii}|F^0\rangle M^{(0)}\ ,
\tag{41}
$$

$$
{}^{\mathrm{IV}}D^{\mu(1)}=E^{\mu(1)}_{\mathrm{HL}}+{}^{\mathrm{IV}}D^{\mu(0)}(M^{(1)}-1)-2\epsilon^{(2)}M^{(0)}-2\,\mathrm{Re}\langle F^0|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})\hat{e}^{\mu}_{ii}|G^{(1)}\rangle M^{(0)},
\tag{42}
$$

$$
\begin{aligned}
{}^{\mathrm{IV}}D^{\mu(2)}=&\,{}^{\mathrm{IV}}D^{\mu(0)}(M^{(2)}-M^{(1)2})+{}^{\mathrm{IV}}D^{\mu(1)}M^{(1)}+\epsilon^{(2)}[M^{(0)}(1+M^{(1)})-1]-\tfrac{3}{2}\epsilon^{(3)}M^{(0)} \\
&+\{2\,\mathrm{Re}\langle F^0|\hat{e}^{\mu}_{ii}\hat{V}_1\hat{e}^{\mu}_{ii}|G^{(1)}\rangle-\langle G^{(1)}|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})\hat{e}^{\mu}_{ii}|G^{(1)}\rangle-2\,\mathrm{Re}\langle F^0|\hat{e}^{\mu}_{ii}(\hat{V}_1-E^{\mu(1)}_{\mathrm{HL}})\hat{e}^{\mu}_{ii}|G^{(2)}\rangle\}M^{(0)},
\end{aligned}
\tag{43}
$$

$$
\begin{aligned}
{}^{\mathrm{IV}}D^{\mu(3)}=M^{(0)}\{&\langle F^0|\hat{e}^{\mu}_{ii}\hat{V}_1(1-\hat{e}^{\mu}_{ii})|G^{(3)}\rangle+\langle G^{(3)}|\hat{e}^{\mu}_{ii}\hat{V}_1(1-\hat{e}^{\mu}_{ii})|F^0\rangle+\langle G^{(1)}|\hat{e}^{\mu}_{ii}\hat{V}_1(1-\hat{e}^{\mu}_{ii})|G^{(2)}\rangle+\langle G^{(2)}|\hat{e}^{\mu}_{ii}\hat{V}_1(1-\hat{e}^{\mu}_{ii})|G^{(1)}\rangle \\
&+\langle G^{(1)}|\hat{e}^{\mu}_{ii}\hat{V}_1\hat{e}^{\mu}_{ii}|G^{(1)}\rangle+2\,\mathrm{Re}\langle F^0|\hat{e}^{\mu}_{ii}\hat{V}_1\hat{e}^{\mu}_{ii}|G^{(2)}\rangle\}+M^{(1)}\,{}^{\mathrm{IV}}D^{\mu(2)}+(M^{(2)}-M^{(1)2})\,{}^{\mathrm{IV}}D^{\mu(1)} \\
&-2M^{(0)}\,{}^{\mathrm{IV}}D^{\mu(0)}\,\mathrm{Re}(\langle F^0|\hat{e}^{\mu}_{ii}|G^{(3)}\rangle+\langle G^{(1)}|\hat{e}^{\mu}_{ii}|G^{(2)}\rangle)\,.
\end{aligned}
\tag{44}
$$

Note that since $\epsilon^{(1)}=0$, ${}^{\mathrm{IV}}E^{\mu(1)}={}^{\mathrm{IV}}D^{\mu(1)}$. Thus, we have ${}^{\mathrm{IV}}E^{\mu(0)}\neq\epsilon^0$ and ${}^{\mathrm{IV}}E^{\mu(1)}\neq E^{\mu(1)}_{\mathrm{HL}}$, i.e., conditions (I.26a) and (I.26c) are not satisfied.

We do not believe that the expansion of ${}^{\mathrm{IV}}E^{\mu}(\lambda)$ should be more rapidly convergent than the two that we first derived. It is, however, one of the many different energy expressions that one can write down. It is no less valid than the first two. The three different sets of energy expansion coefficients $E^{\mu(n)}$ that we have derived, merely show that no special significance should be attached to these coefficients.

The formula for ${}^{\mathrm{IV}}E^{\mu(1)}$ depends explicitly on $G^{(1)}$, and that for ${}^{\mathrm{IV}}E^{\mu(2)}$, on $G^{(2)}$. It appears to be characteristic of the ${}^{\mathrm{IV}}E^{\mu}(\lambda)$ expansion, that the $n$th-order energy depends on the $n$th-order function.

We conclude that three of the four energy expressions considered in Sec. IV of I are not identical functions of $\lambda$. The three merely intersect when $\lambda=1$.

## V. DISCUSSION

There are three insights provided by the EPT we have outlined in this paper: (a) The primitive function $G$ is least distorted from $F^0$. (b) The screened potential which distorts $F^0$ into $G$ is the weakest potential consistent with (a) and the constraint (I.3), namely, $\hat{e}^{\mu}_{ii}G=\Psi^{\mu}_{\alpha i}\langle\Psi^{\mu}_{\alpha i}|G\rangle$. (c) From (b), we infer that this EPT is best suited for use in problems in which the unscreened interaction is strong.

The advantage we see of the EL LW EPT over the original Eisenschitz-London theory and theories giving the same first-order primitive function,[3-6] is that the EL LW EPT offers the insights listed above. Fortunately, this advantage is won without the EL LW perturbation equations becoming much more complicated than those of the other EL-type EPT's. In ease of use, we find no significant difference between the theories.


## ACKNOWLEDGMENT

One of us (W.H.A.) had several stimulating discussions of exchange perturbation theory with Dr. D. M. Chipman. These discussions forced us to reconsider and finally to see more clearly the limitations of the EL LW EPT.

*Based in part on the thesis presented by E. E. Polymeropoulos to Rutgers University in partial fulfillment of the Ph.D. requirements.

†Present address: Max-Planck-Institut für biophysikalische Chemie, Am Fassberg, 34- Göttingen-Nikolausberg, Germany.

‡Work supported in part by the Cities Service Corporation.

[1]W. H. Adams and E. E. Polymeropoulos, preceding paper, Phys. Rev. A 17, 11 (1978). The definitions of the symbols and abbreviations used here are given in paper I.

[2]R. Eisenschitz and F. London, Z. Phys. 60, 491 (1930).

[3]J. N. Murrell and G. Shaw, J. Chem. Phys. 46, 1968 (1967).

[4]J. I. Musher and A. T. Amos, Phys. Rev. 164, 31 (1967); A. T. Amos and J. I. Musher, Chem. Phys. Lett. 1, 149 (1967).

[5]A. van der Avoird, J. Chem. Phys. 47, 3649 (1967); Chem. Phys. Lett. 1, 411 (1967).

[6]J. O. Hirschfelder, Chem. Phys. Lett. 1, 363 (1967).

[7]P. R. Certain, J. O. Hirschfelder, W. Kolos, and L. Wolniewicz, J. Chem. Phys. 49, 24 (1968); J. O. Hirschfelder and P. R. Certain, Int. J. Quantum Chem. S2, 125 (1968).

[8]D. M. Chipman and J. O. Hirschfelder, J. Chem. Phys. 59, 2838 (1973).

[9]J. D. Bowman, Ph.D. thesis (University of Wisconsin, 1972) (unpublished).

[10]P. R. Certain, J. Chem. Phys. 49, 35 (1968); R. J. Damburg and R. Kh. Propin, J. Chem. Phys. 55, 612 (1971).

[11]P. R. Certain, J. O. Hirschfelder, and S. T. Epstein, Chem. Phys. Lett. 4, 401 (1969).

[12]J. H. Epstein, S. T. Epstein, and C. M. Rosenthal, Chem. Phys. Lett. 6, 551 (1970).

[13]A. T. Amos, Chem. Phys. Lett. 5, 587 (1970).

[14]R. E. Peierls, Proc. R. Soc. A 333, 157 (1973).

[15]A. Mann, Chem. Phys. Lett. 32, 363 (1975).

[16]D. M. Chipman, J. D. Bowman, and J. O. Hirschfelder, J. Chem. Phys. 59, 2830 (1973).