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Exchange perturbation theory. IV. Calculations on H_2^+ ^{a)}

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We have applied the two localized-wave-function (LW) exchange-perturbation-theories (EPT) which we have proposed, to the $1s\sigma_g$ and $2p\sigma_u$ states of H_2^+ with the objective of verifying the insights gained from these EPT's and of testing their accuracy. The one LW EPT determines a *primitive* wave function identical to that of the Eisenschitz-London EPT through first order, but which differs from it in all higher orders. The other determines a function identical to that of the Hirschfelder-Silbey EPT through first order and through infinite order, but which differs from it through all intermediate orders. We find that in terms of the perturbation expansion of the interaction energy through third order, our EPT's are as accurate as the original EPT's to which they are related. The LW EPT's have the conceptual asset that their primitive wave functions are *least distorted* from the zero order wave function in a precisely defined sense. We have also calculated interaction energies using the integrals which define the interaction energies in terms of LW's, and substituting the LW's approximated by sums through first, second, and third order. The energies generally increase in accuracy as the LW is summed to higher orders. When each order contribution to the LW is multiplied by a weight which is determined to minimize the interaction energy, and the LW is summed through third order, the interaction energy is in error by 0.07% or less for nuclear separations ranging from 1.0 to 10.0 bohr. An examination of the LW's shows how the optimization procedure works. Other quantities are calculated which show that the LW EPT's are systematically refinable methods for the calculation of LW's as well as for the calculation of interaction energies. This is important because LW's may be used to calculate distinct "physical" contributions to interaction energies.

I. INTRODUCTION

We have shown¹⁻³ that one can gain some insight into the nature of exchange perturbation theories (EPT) by defining the primitive function that one calculates to be least distorted from a product of wave functions for each of the electronic groups (atoms, molecules, shells, etc.) in a system, in the limit that the interactions between groups have been turned off. In this paper we report calculations on H_2^+ which test our insights and which show that our modified Eisenschitz-London² and Hirschfelder-Silbey³ EPT's are not inferior to the originals.^{4,5}

We call the primitive functions used in our studies localized wave functions (LW's). They satisfy an N -electron equation in which the interaction between electronic groups is screened.^{6,7} The screening is more extensive for Eisenschitz-London (EL) type LW's than for Hirschfelder-Silbey (HS) type LW's.¹⁻³ Through first order the EL type LW is identical to the EL primitive function.²⁻⁴ The HS type LW is identical to the HS primitive function⁵ through first order and in infinite order, but not for intermediate orders.³

Many theorists have argued that EPT's are ideally suited to the calculation of interatomic and intermolecular interaction energies.^{1,5,9,17,27} Whether or not any EPT is indeed, a practical tool for this purpose remains to be demonstrated by calculations. However, it is quite clear that if one is to calculate interaction energies by a perturbation theory, that theory must carefully and ex-

plicitly exploit the electronic exchange symmetry.¹ The LW EPT's do just that.

The obligatory test problem for any proposed EPT is H_2^+ . It is a model problem in that the molecular inversion symmetry is exploited rather than electron indistinguishability. It is, however, the one real interatomic interaction problem for which we know exact solutions to the Schrödinger equation. Thus, with H_2^+ one can unambiguously test the accuracy of a proposed EPT. If the EPT fails for H_2^+ , it is not very likely that it will work well for more complex molecules.

Our calculations have been carried out on an exactly soluble model for H_2^+ . We have transformed the LW and EPT equations into finite matrix equations by introducing a basis set of functions consisting of 20 Slater type orbitals, ten centered on each proton. The basis functions were chosen so as to reproduce the exact energies of the $1s\sigma_g$ and $2p\sigma_u$ states within 10^{-5} hartree. This soluble model test has been employed by other workers.⁸⁻¹¹

In the next section we define our notation for H_2^+ and use it to write out the EL and HS type LW equations specifically for H_2^+ . One may use these equations to specialize the LW EPT equations^{2,3} to H_2^+ . We also describe the basis sets and the computer programs we have used.

Section III is concerned with the accuracy through third order of three perturbation expansions of the energy for each of the LW EPT's. It is through these expansions that we are able to make a direct comparison with other EPT's. We have argued, however, that such expansions introduce an unnecessary extra approximation into EPT.¹

In Sec. IV we consider the energy integrals from which the perturbation expansions were derived. These

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integrals have been evaluated with the perturbation expansions of the LW's summed through first, second, and third order. In addition, we have calculated optimized energies with the approximate LW's. We believe the results support our formal argument¹ that the energy should be evaluated without expansion in orders of the perturbation.

A direct check on the accuracy with which LW's may be approximated by perturbation expansions is provided by the calculations described in Sec. V. We compare two properties of LW's calculated by perturbation methods and by direct solution of the matrix representation of the LW equations. These calculations support our formal conclusions¹⁻³ regarding the relative effectiveness of the screening in the HS type and EL type LW EPT's.

Section VI contains a discussion of the properties of primitive functions and LW's in the limit of infinite intersystem separation and a summary of our conclusions.

II. FORMAL AND COMPUTATION DETAILS

This section is concerned with general aspects of the equations solved and how the calculations were done. Some special formal developments are presented in other sections in conjunction with the computed numbers.

The symmetry operation exploited in H_2^+ EPT calculations is inversion, symbolized by \hat{g} . The symmetric and antisymmetric projection operators are

$$\hat{e}^+ = \frac{1}{2}(1 + \hat{g}), \quad \hat{e}^- = \frac{1}{2}(1 - \hat{g}). \quad (1)$$

The zeroth-order Hamilton \hat{H}_1 , wave function F^0 , and energy ϵ^0 are defined as those of a ground state hydrogen atom centered at **a**. In atomic units we have

$$\hat{H}_1 = -\frac{1}{2}\nabla^2 - \frac{1}{r_a}, \quad F^0 = \pi^{-1/2} \exp(-r_a), \quad \epsilon^0 = -\frac{1}{2}. \quad (2)$$

The unscreened perturbation due to a proton at **b**, a distance R from **a**, is

$$\hat{V}_1 = -\frac{1}{r_b}. \quad (3)$$

When we calculate total energies we add in the nuclear repulsion energy of $1/R$. All other quantities in the LW EPT equations are defined in terms of the above operators.

We use G for both the EL and HS type LW's. The EL type LW is obtained by solving²

$$(\hat{H}_1 + \hat{V}_1 - \hat{Q} \hat{V}_1 \hat{Q})G = \epsilon G, \quad (4)$$

with

$$\hat{Q} = 1 - \hat{e}^\mu + \hat{e}^\mu |G\rangle \langle G| \hat{e}^\mu |G\rangle^{-1} \langle G| \hat{e}^\mu. \quad (5)$$

The HS type LW is determined by solving Eq. (4)³ with

$$\hat{Q} = \hat{e}^+ |G\rangle \langle G| \hat{e}^+ |G\rangle^{-1} \langle G| \hat{e}^+ + \hat{e}^- |G\rangle \langle G| \hat{e}^- |G\rangle^{-1} \langle G| \hat{e}^-. \quad (6)$$

Equations (4)–(6) may be used to specialize the LW EPT equations^{2,3} to H_2^+ .

We have solved Eq. (4) and the LW EPT equations by expanding G in a finite basis of nonorthogonal functions. The specific equations solved may be readily written

down by interpreting operators as matrices, and G and the bra-ket symbols as vectors. Since the basis functions are nonorthogonal, one has to introduce the overlap matrix \hat{S} into the equations in exactly the same way in which it is introduced into the Hartree-Fock equations,¹² e.g., using the \hat{Q} defined in Eq. (5), $\hat{V}_1 \hat{Q}$ in the nonorthogonal basis becomes $\hat{V}_1(1 - \hat{e}^\mu) + \hat{V}_1 \hat{e}^\mu |G\rangle \langle G| \hat{e}^\mu \hat{S} |G\rangle^{-1} \langle G| \hat{e}^\mu \hat{S}$.

The basis set consisted of $1s, 1s', 2s, 3s, 2p\sigma, 3p\sigma, 4p\sigma, 3d\sigma, 3d\sigma',$ and $4f\sigma$ Slater type orbitals centered on each proton at $R=1.0, 1.4,$ and 2.0 bohr. At $R=4.0$ and 6.0 bohr a basis of $1s, 1s', 2s, 3s, 2p\sigma, 3p\sigma, 4p\sigma, 3d\sigma, 4d\sigma,$ and $4f\sigma$ was used. At $R=8.0$ and 10.0 bohr we used a $1s, 2s, 3s, 2p\sigma, 3p\sigma, 4p\sigma, 3d\sigma, 3d\sigma', 4d\sigma,$ and $4f\sigma$. The orbital exponents were varied only to the extent necessary to reproduce the exact H_2^+ $1s\sigma_g$ and $2p\sigma_u$ energies to 10^{-5} hartree. We believe the basis was sufficiently large and flexible that if the LW equations were inherently unstable, that instability would have appeared in our calculations.

The integrals needed to form the matrix elements were evaluated using the one-electron integrals part of the BISON program.¹³

The EL and HS type LW's were determined by solving the corresponding LW equations iteratively in the same way that we have described for H_2 .¹⁴ In fact, the H_2^+ program was the prototype for our two electron programs.

The LW EPT equation for the n th order LW, $G^{(n)}$ is of the form

$$(\hat{H}_1 - \epsilon^0 \hat{S})G^{(n)} = \chi^{(n)}, \quad (7)$$

where $\chi^{(n)}$ depends on $\hat{V}_1, F^0, G^{(1)}, \dots, G^{(n-1)}$, etc.¹⁻³ Since the inverse of the matrix $\hat{H}_1 - \epsilon^0 \hat{S}$ does not exist, we have solved the matrix form of Eq. (7) by multiplying the vector $\chi^{(n)}$ by the inverse of the matrix

$$\hat{H}_1 - \epsilon^0 \hat{S} + \epsilon^0 \hat{S} |F^0\rangle \langle F^0| \hat{S}. \quad (8)$$

The level shift matrix $\epsilon^0 \hat{S} |F^0\rangle \langle F^0| \hat{S}$ makes $\hat{H}_1 - \epsilon^0 \hat{S}$ nonsingular, but it has no effect on $G^{(n)}$ since $G^{(n)}$ is orthogonal to F^0 .

The LW EPT program utilizes a subroutine which carries out the projection symbolized by \hat{e}^+ and \hat{e}^- . This allowed us to translate our formulas directly into computer instructions.

In the following sections we use the symbol G for both the HS and EL type LW's. It must be remembered, however, that they are quite different functions. In particular, there is one HS type LW from which one obtains both the $1s\sigma_g$ and $2p\sigma_u$ wave functions by projection, whereas the EL type LW from which the $1s\sigma_g$ function may be projected is quite different from the one which yields the $2p\sigma_u$ function.

III. PERTURBATION EXPANSIONS OF THE INTERACTION ENERGY

The three perturbation expansions of the interaction energy $\Delta E = E_{\text{total}} - \epsilon^0$ that we have evaluated through third order for the EL type and the HS type LW EPT's are derived from the following energy integrals¹⁻³:

TABLE I. The perturbation expansions of the interaction energy^a summed through order n for the $1s\sigma_g$ state.

LW type	Energy formula	Order	R (bohr) = 1.0	2.0	4.0	10.0
HS and EL	IV	0	-51.03	261.98	784.67	77,852.1
HS and EL	I and II	1	-338.90	47.61	20.00	48.49
HS	I	2	56.49	-5.59	1.18	3.05
		3	-19.41	2.72	0.69	0.81
				(4.2) ^b	(0.68) ^c	(0.86) ^c
HS	II	2	78.20	-16.54	-5.53	-2.13
		3	-41.97	6.18	-0.75	-1.92
HS	IV	1	-463.21	97.52	26.34	-58.48
		2	93.54	-21.17	-12.04	-104.19
		3	-4.14	5.18	-0.61	-14.80
EL	I	2	65.97	-6.88	1.85	10.72
		3	-6.04	1.05	0.24	2.44
				(2.6) ^b	(0.23) ^c	(2.56) ^c
EL	II	2	94.63	-18.15	-5.50	-8.12
		3	-9.57	3.64	-1.05	-5.83
EL	IV	1	-466.48	99.19	25.63	-70.74
		2	91.92	-20.99	-8.93	-69.89
		3	-0.12	3.15	-3.61	-30.56

^aIn terms of percent error as defined in Eq. (12).^bReference 8.^cReference 16.

$${}^I E^\mu(\lambda) = \langle F^0 | (\hat{H}_1 + \lambda \hat{V}_1) \hat{e}^\mu | G(\lambda) \rangle \langle F^0 | \hat{e}^\mu | G(\lambda) \rangle^{-1}, \quad (9)$$

$${}^{II} E^\mu(\lambda) = \langle F^0 | \hat{e}^\mu (\hat{H}_1 + \lambda \hat{V}_1) | G(\lambda) \rangle \langle F^0 | \hat{e}^\mu | G(\lambda) \rangle^{-1}, \quad (10)$$

$${}^{IV} E^\mu(\lambda) = \langle G(\lambda) | \hat{e}^\mu (\hat{H}_1 + \lambda \hat{V}_1) \hat{e}^\mu | G(\lambda) \rangle \langle G(\lambda) | \hat{e}^\mu | G(\lambda) \rangle^{-1}. \quad (11)$$

The three integrals become equal in the limit that the expansion parameter $\lambda = 1$ when G has been evaluated exactly. Our calculations show that the energy expansions derived from the integrals can yield quite different numbers.

The energy integral ${}^I E^\mu(\lambda)$ is the one most commonly used in deriving EPT expansions of ΔE . Since the first order HS type LW and the first order EL type LW are identical, respectively, to the HS primitive function and the EL primitive function,¹⁵ our second order energies ${}^I E^\mu$ are identical to the originals. Our third order ${}^I E^\mu$'s, however, differ formally from the originals and may yield quite different results.

We have chosen to report our results for only four of the seven nuclear separations R at which we carried out calculations. We have done this to shorten the paper. The omitted numbers are consistent with those reported here. The R values for which we report results are 1.0 bohr, which represents the region of strong interaction; 2.0 bohr, which is approximately the equilibrium bond length in the H_2^+ ground state; 4.0 bohr, which represents a moderately strong interaction region; and 10 bohr, which represents the weak interaction region.

The results of our calculations are summarized in Tables I and II. Note that we have adopted the standard procedure^{8,9} of expressing the interaction energy in terms of its percentage error relative to the exact energy, i.e., by

$$\text{Percent error} = 100 \times (\Delta E_{\text{exact}} - \Delta E_{\text{approximate}}) / \Delta E_{\text{exact}}, \quad (12)$$

where $\Delta E_{\text{exact}} = E_{\text{exact}} - \epsilon^0$ is the variational energy obtained with our basis set. In this sense we are doing a model calculation even though our variational energies are wrong at most by 10^{-5} hartree. We hope that by doing this we have compensated for some of the differences between the basis sets we have used and those used by other investigators.⁸⁻¹¹

In both tables a zero order interaction energy has been given only for the energy integral IV. This is because $\Delta^I E^{(0)} = \Delta^{II} E^{(0)} = 0$. With one exception, $\Delta^{IV} E^{(0)}$ is badly in error. The error increases with increasing R . The higher order contributions to $\Delta^{IV} E$ are generally large and cause $\Delta^{IV} E$ to jump about. At all but $R = 10.0$ bohr, $\Delta^{IV} E$ summed through third order is acceptably accurate. However, the calculation of $\Delta^{IV} E$ to n th order requires the calculation of the LW to n th order. We conclude that $\Delta^{IV} E$ is not a useful definition of the energy for developing a perturbation expansion even though on formal grounds it is acceptable.

We have verified that $\Delta^I E$ through second order gives, respectively, for the HS and EL type LW's the same values as obtained with the HS and EL primitive functions to an accuracy consistent with the differences between the basis sets.^{8,16} In the tables, we have included in parentheses just below the $\Delta^I E$'s through third order the results obtained by others using the original HS and EL EPT's. The differences between the LW and the original EPT results are generally small. We conclude that the LW EPT's are to this order as accurate as the original EPT's. It should be noted that $\Delta^I E$ and $\Delta^{II} E$ through third order can be calculated if the EL type LW or the EL primitive function is known through first order.^{2,15(b)}

TABLE II. The perturbation expansion of the interaction energy^a summed through order n for the $2p\sigma_u$ state.

LW type	Energy formula	Order	R (bohr) = 1.0	2.0	4.0	10.0
HS and EL	IV	0	-2.19	-91.82	-749.95	-455086.
HS and EL	I and II	1	-11.78	-2.01	-1.22	-201.56
HS	I	2	-7.21	-1.94	0.69	2.92
		3	6.31	-0.30	0.08	2.28
				(-0.3) ^b	(0.13) ^c	(2.18) ^c
HS	II	2	-21.90	-14.91	-7.65	-27.39
		3	29.20	6.33	-1.80	-13.78
HS	IV	1	10.33	-4.20	-28.25	-351.64
		2	63.72	29.99	14.95	320.78
		3	-25.04	-5.19	-0.45	-35.91
EL	I	2	-0.80	-0.41	-0.14	-42.02
		3	-1.76	-0.13	-0.02	-9.04
				(-0.1) ^b	(-0.03) ^c	(-9.06) ^c
EL	II	2	9.41	0.87	0.49	37.91
		3	-1.37	0.33	0.12	24.01
EL	IV	1	41.30	16.52	-13.01	-345.50
		2	-4.10	2.83	-0.89	113.85
		3	0.74	0.94	-0.01	75.56

^aIn terms of percent error as defined in Eq. (12).^bReference 8.^cReference 16.

The HS ΔE 's require the second-order functions for their calculation.

For both the HS and EL type LW's, $\Delta^I E$ is more accurate than $\Delta^{II} E$ in all but one calculation. On formal grounds, we see no reason to expect this.

It can be seen that for $R \leq 4.0$ bohr, $\Delta^I E$ calculated through third order with the EL type LW is generally more accurate than $\Delta^I E$ calculated with the HS type LW. This is consistent with our argument³ that when the interaction is strong, the EL type EPT should work better than the HS type EPT because in the former the screening of \hat{V}_1 is more complete.

When the interaction \hat{V}_1 is weak, i.e., for large R , we have argued³ that the HS type EPT should be more rapidly convergent. This is consistent with the results for $R = 10.0$ bohr. The relatively large error in $\Delta^I E$ calculated with the EL type LW at $R = 10.0$ bohr is found with the original EL EPT, too.⁸

We conclude on the basis of our calculations and of published calculations⁸ that if one wants to calculate ΔE by a perturbation expansion through third order, the LW EPT's will generally do as well as any other EPT. We do not, however, believe that ΔE should be calculated in this way for reasons we have already given.¹ The results of the next section are consistent with our belief.

IV. INTERACTION ENERGIES FROM ENERGY INTEGRALS

We have proposed¹ that interaction energies be calculated using the energy integrals given in Eqs. (9) and (10). The numbers in Tables III and IV provide the first test of this proposal. Energies which are optimized in

the manner explained below have also been calculated.

The energy integrals were evaluated with $\lambda = 1$. In this limit, ${}^I E^\mu = {}^{II} E^\mu$ because \hat{e}^μ and $\hat{H}_1 + \hat{V}_1$ commute, and $(\hat{e}^\mu)^2 = \hat{e}^\mu$.

The energy integrals ${}^I E^\mu$ and ${}^{II} E^\mu$ were simplified^{2,3} to

$${}^I E^\mu = \epsilon^0 + \langle F^0 | \hat{V}_1 \hat{e}^\mu | G \rangle \langle F^0 | \hat{e}^\mu | G \rangle^{-1}, \quad (13)$$

$${}^{II} E^\mu = \epsilon + \langle G | \hat{e}^\mu \hat{V}_1 | G \rangle \langle G | \hat{e}^\mu | G \rangle^{-1}, \quad (14a)$$

$$\epsilon = \langle G | H_1 | G \rangle \langle G | G \rangle^{-1}. \quad (14b)$$

If G is calculated exactly, then ${}^I E^\mu = {}^{II} E^\mu$. We have evaluated the integrals by substituting

$$G[n] = F^0 + G^{(1)} + \dots + G^{(n)} \quad (15)$$

for $G = G[\infty]$. We write for the interaction energies

$$\Delta^I E^\mu[n] = \langle F^0 | \hat{V}_1 \hat{e}^\mu | G[n] \rangle \langle F^0 | \hat{e}^\mu | G[n] \rangle^{-1}, \quad (16)$$

$$\Delta^{II} E^\mu[n] = \epsilon[n] - \epsilon^0 + \langle G[n] | \hat{e}^\mu \hat{V}_1 | G[n] \rangle \langle G[n] | \hat{e}^\mu | G[n] \rangle^{-1}, \quad (17a)$$

$$\epsilon[n] = \langle G[n] | \hat{H}_1 | G[n] \rangle \langle G[n] | G[n] \rangle^{-1}. \quad (17b)$$

These expressions may be derived from the perturbation expansions through infinite order by selectively summing terms so as to reconstruct the denominators $\langle F^0 | \hat{e}^\mu | G \rangle$, $\langle G | \hat{e}^\mu | G \rangle$, and $\langle G | G \rangle$. Note that in what follows we omit the superscripts I and II from ΔE^μ when a statement is true for both $\Delta^I E^\mu$ and $\Delta^{II} E^\mu$.

The first comparison that we make is between $\Delta E^\mu(3)$, the perturbation expansions summed through third order, and $\Delta E^\mu[1]$. This is a reasonable comparison to make for both EL energies because one needs only $G^{(1)}$ to calculate $E^\mu(3)$. On the other hand, to calculate $E^\mu(3)$ with the HS type LW, one must use $G^{(1)}$ and $G^{(2)}$, or both the

TABLE III. The interaction energy^{a,b} of the $1s\sigma_g$ state calculated with the localized wave function summed through order n .

LW type	Energy formula	Order	R (bohr) = 1.0	2.0	4.0	10.0
HS and EL	I and II	0	-338.90	47.61	20.00	48.49
		1	-71.60	-7.27	1.27 (2) ^b	3.06 (3) ^b
HS	I	2	-10.94	1.70	0.57 (4)	0.82 (4)
		3	-34.79	1.40	0.22 (4)	0.28 (5)
		1	-99.57	6.90	0.46 (4)	0.44 (3)
HS	II	2	-31.89	1.28	0.03 (6)	0.02 (5)
		3	-3.94	0.09	0.00 (8)	0.00 (9)
		1	-56.12	4.16	0.42 (5)	0.28 (4)
HS	opt	2	-2.66	0.16	0.01 (7)	0.00 (9)
		3	-0.07	0.00	0.00 (8)	0.00 (9)
		1	73.88	-8.09	1.89 (2)	10.74 (2)
EL	I	2	-0.92	0.44	0.16 (3)	2.44 (3)
		3	-27.09	1.33	0.12 (4)	0.57 (4)
		1	-96.53	6.79	0.50 (3)	2.45 (3)
EL	II	2	-28.82	1.23	0.02 (4)	0.13 (5)
		3	-2.98	0.07	0.00 (5)	0.01 (7)
		1	-53.62	3.83	0.38 (3)	0.12 (5)
EL	opt	2	-2.17	0.11	0.02 (4)	0.00 (8)
		3	-0.02	0.00	0.00 (5)	0.00 (8)

^aIn terms of percent error as defined in Eq. (12).^bNumbers in parentheses indicate the order in the energy to which the HS and EL van der Avoird-Hirschfelder expansions must be carried to obtain results comparable or slightly better than the integral results in this work.TABLE IV. The interaction energy^{a,b} of the $2p\sigma_u$ state calculated with the localized wave function summed through order n .

LW type	Energy formula	Order	R (bohr) = 1.0	2.0	4.0	10.0
HS and EL	I and II	0	-11.78	-2.01	-1.22	-201.57
		1	-8.70	-1.95	0.70 (2) ^b	3.00 (2) ^b
HS	I	2	-1.22	-0.11	0.06 (4)	2.30 (3)
		3	0.24	-0.11	0.04 (5)	1.13 (4)
		1	-6.39	-2.07	-0.52 (3)	-0.18 (6)
HS	II	2	-0.15	-0.08	-0.04 (5)	-0.03 (9)
		3	-0.04	-0.01	-0.00 (7)	-0.00 (11)
		1	-0.10	-1.99	-0.04 (5)	-0.13 (7)
HS	opt	2	-0.02	-0.04	-0.03 (5)	-0.00 (11)
		3	-0.01	-0.00	-0.00 (7)	-0.00 (11)
		1	-2.86	-0.46	-0.14 (2)	-42.02 (2)
EL	I	2	-1.02	-0.14	-0.02 (3)	-9.03 (3)
		3	-0.82	-0.05	-0.00 (4)	-1.99 (4)
		1	-0.70	-0.11	-0.03 (3)	-9.10 (3)
EL	II	2	-0.08	-0.01	-0.00 (4)	-0.45 (5)
		3	-0.07	-0.00	-0.00 (4)	-0.02 (7)
		1	-0.06	-0.00	-0.01 (4)	-0.55 (5)
EL	opt	2	-0.00	-0.00	-0.00 (4)	-0.00 (8)
		3	-0.00	-0.00	-0.00 (4)	-0.00 (8)

^aIn terms of percent error as defined in Eq. (12).^bNumbers in parentheses indicate the order in the energy to which the HS and EL van der Avoird-Hirschfelder expansions must be carried to obtain results comparable or slightly better than the integral results in this work.

HS and EL $G^{(1)}$'s.⁸ Whether this should make the HS third order energy more or less accurate relative to the EL third order energy is not clear to us. We believe that the reader should be aware of this point, but that it is not particularly important.

The comparison of the $\Delta E^\mu(3)$ from Table I and II, respectively, with the $\Delta E^\mu[1]$ of Tables III and IV reveals some large differences with both HS and EL type LW's. Since $\Delta E^\mu(3)$ is essentially an approximation to $\Delta E^\mu[1]$, the large differences show that it is not a consistently good approximation. Even when the difference between $\Delta E(3)$ and $\Delta E[1]$ is relatively small, the error relative to the exact ΔE can be large. To us this means that one can not trust ΔE 's calculated with only F^0 and $G^{(1)}$, even when different energy formulas give almost identical numbers.

We have calculated $G^{(2)}$ and $G^{(3)}$ in order to see if they improve, respectively, $G[1]$ and $G[2]$. Note that $\Delta^I E[2]$ is more accurate than $\Delta^I E[3]$ at small R , whereas $\Delta^{II} E[n]$ is always more accurate than $\Delta^{II} E[n-1]$. The explanation for this is that $\Delta^{II} E[n]$ is an upper bound to the exact ΔE for both states, whereas $\Delta^I E$ is not. At the larger R values $\Delta E[n]$ is always more accurate than $\Delta E[n-1]$. On the basis of the $\Delta^{II} E[n]$ we can say that $G[n]$ is a better approximation to $G[\infty]$ than is $G[n-1]$, and that in this practical sense the perturbation expansion is converging for both the HS and EL type LW's.

It is interesting to compare the EL ΔE 's at $R=10.0$ bohr. Note that $\Delta^I E^\mu[1]$ is significantly in error for both states. This is just what one expects due to the very incorrect weight with which R^{-4} enters the asymptotic $1/R$ expansion of the EL $\Delta^I E^\mu[1]$.^{8,19,20} Note that $\Delta^{II} E^\mu[1]$ is significantly more accurate than $\Delta^I E^\mu[1]$. This is also just what one expects on the basis of the asymptotic $1/R$ expansion of $\Delta^{II} E^\mu[1]$.^{8,19,20} That $\Delta^I E^\mu[2]$ is more accurate than $\Delta^I E^\mu[1]$ and that $\Delta^{II} E^\mu[2]$ is more accurate than $\Delta^I E^\mu[2]$ and $\Delta^{II} E^\mu[1]$ at $R=10.0$ bohr are also consistent with the $1/R$ expansions.^{19,20} The expansions and our calculations suggest that $\Delta^{II} E^\mu$ is more trustworthy at large R than is $\Delta^I E^\mu$.

Wave functions and energies calculated by perturbation methods can generally be improved by variational methods.¹⁷ Chipman and Hirschfelder⁸ found that minimizing, in our notation, the energy expectation value $\langle \gamma F^0 + G^{(1)} | \hat{e}^\mu (\hat{H}_1 + \hat{V}_1) | \gamma F^0 + G^{(1)} \rangle \langle \gamma F^0 + G^{(1)} | e^\mu | \gamma F^0 + G^{(1)} \rangle^{-1}$ with respect to γ gave very accurate results in H_2^+ . We have made the obvious extension. We define

$$G_w[n] = F^0 + \sum_{j=1}^n w_j[n] G^{(j)} \quad (18)$$

and extremalize

$$E_w^\mu[n] = \langle G_w[n] | \hat{e}^\mu \hat{H} | G_w[n] \rangle \langle G_w[n] | \hat{e}^\mu | G_w[n] \rangle^{-1} \quad (19)$$

with regard to the $w_j[n]$. In this way we have obtained the results labeled "opt" in Tables III and IV. Note that if the optimized function $G_{\text{opt}}[n]$, i.e., $G_w[n]$ with the energy extremalizing set of $w_j[n]$'s, is substituted for $G[n]$ in $\Delta^I E[n]$, the result must be identical to the energy obtained with Eq. (19), i.e., $E_{\text{opt}}^\mu[n]$.¹⁸

The results we have obtained for $\Delta E_{\text{opt}}^\mu[1]$ with HS and

TABLE V. Effective weight of $G^{(1)}$ in the Eisenschitz-London type $G[n]$ and $G_{\text{opt}}[n]$.

State	Weight	$R(\text{bohr}) = 1.0$	2.0	4.0	10.0
$1s\sigma_g$	$w_1[1]$	0.695	0.789	1.083	1.281
	$w_1(2)$	0.592	0.714	1.051	1.214
$2p\sigma_u$	$w_1[1]$	1.417	1.308	1.118	1.260
	$w_1(2)$	1.006	1.156	1.091	1.200
$1s\sigma_g$	$w_1^T[2]$	0.679	0.765	1.054	1.276
	$w_1(3)$	0.612	0.747	1.000	1.226
$2p\sigma_u$	$w_1^T[2]$	1.063	1.225	1.106	1.253
	$w_1(3)$	0.921	1.201	1.103	1.241

EL type LW's are almost identical to those obtained by Chipman and Hirschfelder.⁸ The differences probably arise from the quite different basis sets used in the two studies. It should be noted that for the $1s\sigma_g$ state at $R=1.0$ bohr, $\Delta E_{\text{opt}}^\mu[1]$ is quite poor. Chipman's ΔE was also poor at $R=1.0$ bohr.¹⁹

The results we have obtained with $\Delta E_{\text{opt}}^\mu[2]$ are good to excellent. The results with $\Delta E_{\text{opt}}^\mu[3]$ are uniformly excellent.

It is interesting to compare the accuracy of the interaction energies calculated with the energy integrals to those calculated with higher order energy expansions.¹⁶ In Tables III and IV the numbers in parentheses in the $R=4.0$ and 10.0 columns indicate the order in the energy to which the HS and EL van der Avoird-Hirschfelder ΔE expansions must be carried to obtain results comparable to or a little better than our integral results. Although it is not generally possible with EPT's to calculate with the zeroth- through n th-order functions the energy through $(2n+1)$ th-order, we can use $2n+1$ as a rough measure of the success or failure of the integral formulas. It can be seen that the energy integrals evaluated with $G[n]$ are not generally equal in accuracy to a perturbation expansion of ΔE to $(2n+1)$ th order. The optimized energies, however, are generally of greater accuracy than $\Delta E(2n+1)$ when the error in ΔE is significant.

The energy calculated with $G_{\text{opt}}[n]$ is in most cases as accurate or more accurate than that calculated with $G[n+1]$. This may be understood for the EL type functions in the following way. We may resolve $G^{(2)}$ into a component orthogonal to $G^{(1)}$, call it $\bar{G}^{(2)}$, and a component equal to $G^{(1)}$ multiplied by $\langle G^{(1)} | G^{(2)} \rangle \langle G^{(1)} | G^{(2)} \rangle^{-1}$. Thus, $G[2]$ differs from $G[1]$ essentially by the addition of $\bar{G}^{(2)}$ and the change of the weighting of $G^{(1)}$ from 1 in $G[1]$ to

$$w_1(2) = 1 + \langle G^{(1)} | G^{(2)} \rangle \langle G^{(1)} | G^{(1)} \rangle^{-1}. \quad (20)$$

One can see from Table V that $w_1[1]$ is more nearly equal to $w_1(2)$ than to 1. We have also resolved $G^{(3)}$ into a component orthogonal to $G^{(1)}$ and one proportional to $G^{(1)}$, and calculated the weight with which $G^{(1)}$ contributes to $G[3]$, namely,

$$w_1(3) = 1 + (\langle G^{(1)} | G^{(2)} \rangle + \langle G^{(1)} | G^{(3)} \rangle) \langle G^{(1)} | G^{(1)} \rangle^{-1}. \quad (21)$$

This weight can be compared in Table V to $w_1[1]$ and to

TABLE VI. The distortion energy^a $\epsilon - \epsilon^0$ summed through order n .

State	LW type	n	R (bohr) = 1.0	2.0	4.0	10.0
$1s\sigma_g$ and $2p\sigma_u$	HS	2	-21.86	-14.41	9.55	6.58
		3	18.87	20.12	8.86	1.64
		4	15.14	0.32	3.14	0.44
		∞^b	0.147859	0.037890	0.006165	0.000249
$1s\sigma_g$	EL	2	-47.37	-34.12	18.31	39.49
		3	10.70	10.78	3.51	12.89
		4	21.41	1.50	1.49	3.91
		∞^b	0.123093	0.033074	0.006086	0.000181
$2p\sigma_u$	EL	2	40.98	41.05	22.36	37.46
		3	24.04	16.89	5.24	11.61
		4	18.29	7.19	1.20	3.32
		∞^b	0.012328	0.001870	0.000305	0.000126

^aAll energies to finite orders in terms of percent error as defined in Eq. (12).

^bEnergy in hartree.

the total weight with which $G^{(1)}$ contributes to $G_{\text{opt}}[2]$, namely,

$$w_1^T[2] = w_1[1] + w_2[2] \langle G^{(1)} | G^{(2)} \rangle \langle G^{(1)} | G^{(1)} \rangle^{-1}. \quad (22)$$

The numbers show that adding $G^{(n+1)}$ to $G[n]$ to get $G[n+1]$ has essentially the same effect on the total weight with which $G^{(1)}$ contributes to G , as does optimizing the energy with respect to the $w_j[n]$.

An analysis similar to the one above for $G^{(1)}$ has been carried out by us with respect to the component of $G^{(2)}$ which is orthogonal to $G^{(1)}$. The results are consistent with those for $G^{(1)}$.

We conclude from the above analysis that the major effect of adding $G^{(n+1)}$ to $G[n]$ to get $G[n+1]$ for $n=1$ and 2 is to change the weights with which $G^{(1)}$ and $\bar{G}^{(2)}$ contribute to G .

A similar analysis is not appropriate for the HS type LW's. The HS type LW is independent of the symmetry μ whereas the EL type LW is not. When we extremalize the energy of the symmetry state μ with a HS type $G_w[n]$, we may be getting a better approximation to that symmetry component of G , but it is not likely that we are improving the other components as well. In contrast, the above analysis shows for the EL type LW's that $G_{\text{opt}}[n]$ is a better approximation to $G[\infty]$ than is $G[n]$ in that optimization of $G_w[n]$ has caused $G^{(1)}$ and $\bar{G}^{(2)}$ to contribute with weights comparable to those with which they contribute to $G[n+1]$.

From our calculations it appears that energy optimization with $G_w[n]$ produces in most cases a significant improvement in the calculated interaction energies. We have found that energy optimization involves little extra effort compared to the work that goes into calculating the $G^{(n)}$. It was also remarked by Chipman and Hirschfelder⁸ that calculating $\Delta E_{\text{opt}}^\mu[1]$ is not much more difficult than calculating $\Delta E^\mu(3)$. In the EL case, the same integrals are used in evaluating $\Delta E^\mu(3)$ as are used in the optimization calculation. In the HS case, $\Delta E^\mu(3)$ requires the evaluation of $G^{(2)}$ in addition to $G^{(1)}$, but the integrals used in $\Delta E^\mu(3)$ and $\Delta E^\mu[1]$ are of comparable difficulty. The evaluation of $\Delta E_{\text{opt}}^\mu[2]$ and $\Delta E_{\text{opt}}^\mu[3]$

should be comparable in difficulty to calculating $\Delta E^\mu(5)$ and $\Delta E^\mu(7)$.

The calculations described in this section show that the LW EPT's are in effect systematically refinable procedures for calculating interaction energies at small, intermediate, and large interatomic distances.

V. ACCURACY OF THE PERTURBATION APPROXIMATION TO THE LOCALIZED WAVE FUNCTION

We have pointed out that LW's can be used to assess quantitatively the degree to which a system is *separable* into weakly interacting groups²¹ and to analyze the interaction energy into physically understandable contributions²² in the manner of Heitler and London.²³ For this reason we are interested in the accuracy to which the HS type and EL type LW EPT's produce approximate LW's. There are two LW properties whose accuracy we have studied for H_2^+ .

The first LW property is the distortion energy $\epsilon - \epsilon^0$. This quantity is minimized by G under the constraints appropriate to the EL and HS type EPT's. It is always positive. In Table VI we give the percent error in $\Delta\epsilon(n) = \epsilon^{(1)} + \dots + \epsilon^{(n)}$ relative to the exact $\epsilon - \epsilon^0$ obtained by solving the LW equation iteratively. The exact value is labeled by ∞ in the table. Note that $\epsilon^{(1)}$ is identically zero and thus, as an approximation to $\epsilon - \epsilon^0$, it is always 100% in error. Also, the error in $\Delta\epsilon(n)$ is smaller in magnitude than that in $\Delta\epsilon(n-1)$ in all but two cases. The two exceptions occur when the perturbation is strong, namely, at $R=2.0$ bohr for the HS type LW and at $R=1.0$ bohr for the EL type $1s\sigma_g$ LW.

The second LW property we consider is $\|\chi[n]\|^2 = \langle G[n] - F^0 | G[n] - F^0 \rangle$. This quantity is interesting because it gives equal weight to all points of the physical space where $\epsilon - \epsilon^0$ weights points more heavily the closer they are to the two protons. We have calculated $\|\chi[\infty]\|^2$ using the exact G , i.e., the G we found by solving the LW equation iteratively. In Table VII we give the percent error $100 \times (\|\chi[\infty]\|^2 - \|\chi[n]\|^2) / \|\chi[\infty]\|^2$ for $n=1, 2$, and 3, and the value of $\|\chi[\infty]\|^2$.

One can see from the first 12 rows of Table VII that at $R=10.0$ bohr the HS and EL type LW EPT's give improved values of $\|\chi[n]\|^2$ for each increase in n . At $R=4.0$ bohr, the $1s\sigma_g$ EL $\|\chi[3]\|^2$ is a little less accurate than $\|\chi[2]\|^2$. At $R=1.0$ and 2.0 bohr, $\|\chi[3]\|^2$ is, with one exception, less accurate than $\|\chi[2]\|^2$. This shows that if the perturbation expansions of G are converging as most of our calculations suggest, they are not converging monotonically.

The last six rows of Table VII contain the percent error in $\|\chi_{\text{opt}}[n]\|^2 = \langle G_{\text{opt}}[n] - F^0 | G_{\text{opt}}[n] - F^0 \rangle$ for the EL type LW. We defined $G_{\text{opt}}[n]$ in Sec. IV and considered its relation to the EL $G[n]$. One can see from Table VII that the optimization procedure gives an approximate LW of increasing accuracy with increasing n . Note, however, that the magnitude of the error in $\|\chi_{\text{opt}}[n]\|^2$ is larger than the error in the corresponding $\|\chi[n]\|^2$ at $R=1.0$ bohr for $n < 3$ for the $2p\sigma_u$ state. This is not surprising because there is no reason to expect that ex-

TABLE VII. The percent error in $\langle G[n] - F^0 | G[n] - F^0 \rangle$.

State	LW type	n	$R(\text{bohr}) = 1.0$	2.0	4.0	10.0
$1s\sigma_g$ and $2p\sigma_u$	HS	1	-43.97	-39.10	-2.45	6.88
		2	1.22	4.67	5.06	1.38
		3	15.48	6.17	1.78	0.32
		∞^a	0.209032	0.055753	0.010327	0.000589
$1s\sigma_g$	EL	1	-86.89	-59.21	11.68	38.74
		2	4.21	4.08	1.19	9.58
		3	18.34	5.55	1.29	2.30
		∞^a	0.160302	0.049971	0.010070	0.000384
$2p\sigma_u$	EL	1	5.85	34.94	18.75	36.40
		2	-1.72	12.47	2.69	8.41
		3	11.11	4.92	0.44	1.89
		∞^a	0.010129	0.001510	0.000512	0.000238
$1s\sigma_g$	EL(opt)	1	9.66	0.76	-3.64	-0.59
		2	2.67	0.24	0.24	0.10
		3	2.62	0.42	-0.04	0.01
$2p\sigma_u$	EL(opt)	1	-89.17	-11.24	-1.57	-0.95
		2	-17.45	1.08	-0.16	0.05
		3	0.21	0.35	-0.02	0.01

^aActual value rather than percent error.

tremalization of $\Delta E_w^\mu[n]$ with regard to the $w_j[n]$ will make $G_w[n]$ a more accurate approximation to the exact LW. It is interesting, however, that in most cases extremalization of $\Delta E_w^\mu[n]$ has given a more accurate approximate LW.

The data in Tables VI and VII for $n = \infty$ provide a direct check of one insight we have gained by the use of LW's. That insight was that the EL type LW should differ less from F^0 than the HS type LW. Both $\epsilon - \epsilon^0$ and $\langle G - F^0 | G - F^0 \rangle$ can be regarded as measures of the degree to which a LW differs from F^0 . Both measures show that the HS type LW differs from F^0 a little more than does the $1s\sigma_g$ EL type LW and quite a bit more than does the $2p\sigma_u$ EL type LW.

The calculations described in this section support the idea that the LW EPT's provide a systematic procedure for the approximation of LW's as well as interaction energies. This point will be explored further in our H_2 calculations.²⁴

VI. DISCUSSION AND CONCLUSIONS

Kutzelnigg has raised an important question, namely do primitive functions exist for all proposed EPT's such that, as the intersystem distance R increases to infinity, the primitive function goes smoothly to the limit F^0 ?²⁵ This is a question which we should answer with regard to the primitive functions considered in this article.

The HS type LW is identical to the HS primitive wave function in infinite order.³ Kutzelnigg has argued that the HS primitive function is "genuinely" primitive in a precisely defined sense.²⁵ Thus, the HS type LW must also be genuinely primitive.

Whether or not the EL type LW is a genuine primitive function is more difficult to answer. Kutzelnigg has remarked that the EL primitive function is not genuinely primitive. The EL type LW is identical to the EL primitive function only through first order. We have shown that in all higher orders and in infinite order, the EL type LW is not identical to the EL primitive function.²

Thus, the EL type LW could be genuinely primitive even though the EL primitive function is not.

Whether or not the EL type LW satisfies Kutzelnigg's condition for being genuinely primitive, Eqs. (32a) and (32b) of his paper,²⁵ is a question we have not been able to answer. We have, however, a general argument for believing that the EL type LW goes smoothly into F^0 in the limit that $R \rightarrow \infty$.

The EL type LW is obtained by solving Eq. (4) with \hat{Q} defined by Eq. (5). We have shown that the solution to this equation is identical to the function defined in terms of the eigenfunction $\Psi_{\gamma k}^\lambda$ of \hat{H} by the following equations⁷:

$$G^\mu = C_{\alpha i}^\mu \Psi_{\alpha i}^\mu + \sum_\nu \sum_\beta \sum_j (1 - \delta_{\mu\nu} \delta_{ij}) C_{\beta j}^\nu \Psi_{\beta j}^\nu, \quad (23a)$$

$$\epsilon^\mu = \langle G^\mu | \hat{H}_1 | G^\mu \rangle \langle G^\mu | G^\mu \rangle^{-1} = \text{extremal}. \quad (23b)$$

In the above $\Psi_{\alpha i}^\mu$ is the α th function belonging to the i th row of the μ th irreducible representation of the symmetry group of the system. The variational parameters $C_{\gamma k}^\lambda$ are determined by Eq. (23b). Note that G^μ is constrained to contain only one function belonging to the μ th irreducible representation. If, instead, all functions belonging to the μ th irreducible representation are included in Eq. (23a), then Eq. (23b) is satisfied by $G^\mu = F^0$. In this sense, G^μ is *least distorted* from F^0 at all R .

On the basis of the preceding paragraph, it is possible to rephrase the question, does G^μ go to F^0 as R goes to infinity? We can ask, instead, do Eqs. (23a) and (23b) have F^0 as a solution at infinite R ? We have to note here that F^0 may not be a simple product of atomic (molecular, etc.) wave functions, but may instead be a linear combination of degenerate products of atomic functions. If the $\Psi_{\gamma k}^\lambda$ can be written as linear combinations of degenerate F^0 's at infinite R , then Eqs. (23a) and (23b) define G^μ at infinite R to be an F^0 or a linear combination of degenerate F^0 's. We have explicitly shown this to be true for H_2^+ .

The conditions which Kutzelnigg places on functions to make them genuinely primitive are a means of defining primitive functions so that they will have properties we want them to have. The least distortion requirement we impose and Chipman's requirement of *best* localization²⁶ are alternative means of definition. The importance of defining the primitive wave function is illustrated by Kutzelnigg's analysis of his Eqs. (12) and (15), the equations which define the Murrell-Shaw, Musher-Amos²⁷ (MS-MA) primitive function. What Kutzelnigg's Eq. (35) shows is that the MS-MA function is not genuinely primitive because N_μ^{-1} , the weight with which $\Psi_{\alpha i}^\mu$ appears in the primitive function, is undefined by his Eqs. (12) and (15). However, N_μ^{-1} may be defined by the MS-MA perturbation equations, or by the method of solving these equations, such that N_μ^{-1} takes on the one value which will make the MS-MA function genuinely primitive. We have not verified that N_μ^{-1} does take on this value for R infinite. Our point is simply that either an explicit or implicit definition of primitive functions is always needed.

When we initiated the work described in this paper, it was with the idea of complementing the study by Chipman and Hirschfelder.^{8,19} The results presented in Sec. III do just that. Our conclusion is that the LW EPT's work as well as the other EPT's in the important case of H_2^+ , the one physical system for which we know the exact solutions to the Schrödinger equation. The LW EPT's have, however, the conceptual advantage that their primitive functions are *least distorted* from F^0 .

In Sec. IV we have broken new ground by calculating the energy integrals from which the perturbation expansions of the energy are derived. The results support our arguments¹⁻³ that the energy integrals should be used instead of their perturbation expansions. Furthermore, by optimizing $\Delta^{II}E^n[n]$ for $n=1, 2$, and 3 , we have shown that very accurate interaction energies may be calculated for small, intermediate, and large values of R using the LW EPT's.

We have also examined in Sec. IV why the energy optimization procedure works so well. What we have found is that the major effect of $G^{(n)}$ is to change the weights with which $G^{(1)}, \dots, G^{(n-1)}$ contribute to $G^{(n)}$ approximately to the same values as found in $G_{\text{opt}}[n-1]$.

In Sec. V we have examined the accuracy with which the $G[n]$ and $G_{\text{opt}}[n]$ approximate to the exact G 's. The results support the idea that LW's can be calculated by perturbation methods. This is of some importance because LW's can be used to calculate directly such physical contributions to interaction energies, as Coulombic, dispersion, and exchange energies.^{21,22}

To us, our most important conclusion is that the LW EPT's may be added to the list of EPT's⁹⁻¹¹ which may be tentatively regarded as systematically refinable methods for the theoretical study of interacting electronic systems. It is our intention to test further the LW EPT's in applications to systems more complicated than H_2^+ . We are nearly ready to report results for H_2 , we have begun work on HHe^+ , and we are writing the programs needed in the study of systems having more than two electrons. Whether or not the LW EPT's, or any EPT, can be made into a practical computational tool remains to be seen. It is worth noting, however, that the EL type LW EPT can be greatly simplified for systems of four or more electrons without resort to new approximations.²⁸

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