Theor Chim Acta (1992) 84: 37–53

Theoretica Chimica Acta

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Quantum field theoretical methods in chemically bonded systems IV

Analysis of perturbative energy terms for H_2, LiH, FH and F_2*

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Received May 23, 1991/Accepted December 20, 1991

Summary. A new perturbative procedure is analyzed numerically for four single bonded diatomic molecules. The starting model is the second-quantized self-consistent Heitler–London model. The unperturbed function is a four-determinant Bardeen–Cooper–Schrieffer function. The model Hamiltonian is the ordinary Hamiltonian plus linear and quadratic powers of a two-level number operator. Parameters which multiply the additional terms are chosen to enforce particle-number symmetry. Convergence of the perturbative series for the energy as a function of internuclear distance is reasonable: third-order corrections are about an order of magnitude smaller than second-order corrections; total corrections through third order are about two orders of magnitude smaller than first-order energies.

Key words: Perturbative methods – Perturbative analysis curves – H_2 – LiH – FH – F_2 – Single bonds

1. Introduction

Bardeen–Cooper–Schrieffer–Lipkin–Nogami–Heitler–London(N) (BCSLN–HL(N)) is Nth-order many-body perturbation theory (MBPT) starting from the self-consistent (SC) HL model [1]. It is the simplest correct SC MBPT for chemical bonds. The choice of nomenclature is explained in Part I of this series [2].

Spectroscopic constants calculated with BCSLN–HL(3) were reported in Paper I for H_2, LiH, FH, F_2 and N_2. Renormalized Feynman diagrams (FD) are derived in Part II [3]. Part III reports ground-state energy curves for four single

* This work was supported in part by the U.S. Department of the Navy, Space and Naval Warfare Systems Command under Contract N00039-89-C-0001, and in part by IBM RSP 3112. It was presented, in part, at the Midwest Theoretical Chemistry Conference, Indianapolis, Indiana, 1989, and at the Midwest Theoretical Chemistry Conference, Madison, Wisconsin, 1990.

bonded diatomic molecules [4].

$$\left.\begin{array}{ll} H_2(X^1\Sigma_g^+) \to 2H(^2S) & 1a_0 \leqslant R \leqslant 8a_0 \\ LiH(X^1\Sigma^+) \to Li(^2S) + H(^2S) & 2a_0 \leqslant R \leqslant 15a_0 \\ FH(X^1\Sigma^+) \to F(^2P) + H(^2S) & (1.03a_0 \leqslant R \leqslant 9a_0 \\ F_2(X^1\Sigma_g^+) \to 2F(^2P) & 1.8a_0 \leqslant R \leqslant 6a_0 \end{array}\right\}. \tag{1}$$

Reasons for selecting these diatomics are given in Part I of this series.

The present work describes the unperturbed models (BCSLN–HL(1)) and analyzes the perturbative corrections (BCSLN–HL(2 and 3)) which are the basis for the energy curves reported in Part III. Section 2 describes the unperturbed models. Section 3 analyzes the perturbative corrections.

2. BCSLN–HL(1)

2.1. HL *quasiparticles*

Pairing is determined by adiabatic continuity to atomic limits. The hole and particle which become degenerate at long bond distances are *paired levels.*

$$\left.\begin{array}{lll} \textit{bond} & \textit{paired hole} & \textit{paired particle} \\ H_2(X^1\Sigma_g^+) & 1\sigma_g & 1\sigma_u \\ LiH(X^1\Sigma^+) & 2\sigma & 3\sigma \\ FH(X^1\Sigma^+) & 3\sigma & 4\sigma \\ F_2(X^1\Sigma_g^+) & 3\sigma_g & 3\sigma_u \end{array}\right\}. \tag{2}$$

Degeneracy is determined by adiabatic symmetry correlation.

The density matrix (pairing matrix) has diagonal (canonical) form (*canonical representation* [5, p 248]). $\hat{a}_k(\hat{a}_{\bar{k}})$ is an annihilation operator for orbital ϕ_k with spin α (spin β). $\bar{k}$ is shorthand for $-k$. Pairing removes particle-hole degeneracy by diagonalizing a model Hamiltonian. A special Bogoliubov–Valatin (BV) transformation is the transformation to the diagonal representation. Suppose the label 1 (2) is assigned to the hole (particle) which is allowed to pair. The *HLBV transformation* pairs spin quantum numbers for $\hat{a}_1$ and $\hat{a}_2$ and is a particle-hole transformation for all other levels.

$$\left.\begin{array}{l} \left.\begin{array}{ll} \hat{\alpha}_1 = u_1\hat{a}_1 - v_1\hat{a}_{\bar{1}}^+ & \hat{\alpha}_2 = u_2\hat{a}_2 - v_2\hat{a}_{\bar{2}}^+ \\ \hat{\alpha}_{\bar{1}} = u_1\hat{a}_{\bar{1}} + v_1\hat{a}_1^+ & \hat{\alpha}_{\bar{2}} = u_2\hat{a}_{\bar{2}} + v_2\hat{a}_2^+ \end{array}\right\} \textit{ paired levels} \\ \left.\begin{array}{l} \hat{\alpha}_k = \hat{a}_{\bar{k}}^+ \\ \hat{\alpha}_{\bar{k}} = \hat{a}_k^+ \end{array}\right\} \textit{ holes} \\ \left.\begin{array}{l} \hat{\alpha}_k = \hat{a}_k \\ \hat{\alpha}_{\bar{k}} = \hat{a}_{\bar{k}} \end{array}\right\} \textit{ particles} \end{array}\right\}. \tag{3}$$

$\hat{\alpha}_1$ and $\hat{\alpha}_2$ ($\hat{\alpha}_{\bar{1}}$ and $\hat{\alpha}_{\bar{2}}$) describe *HL quasiparticles* with spin α (spin β). Paired holes and particles are fractionally occupied. u_k (v_k) is the weight of the particle (hole) operator in the HL quasiparticle operator $\hat{\alpha}_k$. u_k^2 (v_k^2) is the probability that ϕ_k is empty or particle-like (full or hole-like).

HL quasiparticles depend on overlap and relative phases of HLBV transformation coefficients. The transformation from ϕ_1 and ϕ_2 to overlapping orbitals χ_l and χ_r connects overlap to HLBV transformation coefficients.

$$\left.\begin{aligned}\chi_l &= v_1\phi_1 + u_1\phi_2\\ \chi_r &= v_1\phi_1 - u_1\phi_2\end{aligned}\right\} \quad S = \langle\chi_l|\chi_r\rangle = 2v_1^2 - 1. \tag{4}$$

u_1^2 is determined by the normalization condition:

$$u_1^2 + v_1^2 = 1. \tag{5}$$

v_2^2 is determined by the conservation condition for the two bonding electrons [6]:

$$v_1^2 + v_2^2 = 1. \tag{6}$$

Phase choices fix the HLBV transformation coefficients for the ground state:

$$\left.\begin{aligned}u_1 > 0, \quad v_2 = -u_1\\ v_1 > 0, \quad u_2 = v_1\end{aligned}\right\}. \tag{7}$$

2.1.1. Unperturbed ground state. An *HL pair* is a product of paired annihilation operators for HL quasiparticles.

$$\hat{M} = -\left(\frac{1}{v_1^2}\right)\hat{\alpha}_1\hat{\alpha}_{\bar{1}}\hat{\alpha}_2\hat{\alpha}_{\bar{2}}. \tag{8}$$

Each HL pair is a *model two-electron bond.* A *model core* is a product of unpaired hole operators:

$$\hat{K} = \left\{\begin{array}{ll} 1 & \mathrm{H_2}\\ \hat{a}^+_{1\sigma}\hat{a}^+_{1\bar{\sigma}} & \mathrm{LiH}\\ \prod_{k=1}^{2}\prod_{\zeta=x,y}\hat{a}^+_{k\sigma}\hat{a}^+_{k\bar{\sigma}}\hat{a}^+_{1\pi_\zeta}\hat{a}^+_{1\bar{\pi}_\zeta} & \mathrm{FH}\\ \prod_{p=g,u}\prod_{k=1}^{2}\prod_{\zeta=x,y}\hat{a}^+_{k\sigma_p}\hat{a}^+_{k\bar{\sigma}_p}\hat{a}^+_{1\pi_{\zeta p}}\hat{a}^+_{1\bar{\pi}_{\zeta p}} & \mathrm{F_2}\end{array}\right\}. \tag{9}$$

Each model core describes a closed-shell doubly-charged positive ion.

The product of model pair and core operators applied to the *bare vacuum* $|\ \rangle$ is the unperturbed ground state (*HL vacuum* $|\mathscr{HL}\rangle$):

$$|\mathscr{HL}\rangle = \hat{M}\hat{K}|\ \rangle \tag{10}$$

$$= u_1v_1(\hat{K}|\ \rangle - |\mathbf{1\bar{1}2\bar{2}}\rangle) + v_1^2|\mathbf{1\bar{1}}\rangle - u_1^2|\mathbf{2\bar{2}}\rangle \tag{11}$$

$$= \sqrt{u_1^4 + v_1^4}|\mathrm{HL}\rangle + u_1v_1(\hat{K}|\ \rangle - |\mathbf{1\bar{1}2\bar{2}}\rangle) \tag{12}$$

$$\hat{\alpha}_k|\mathscr{HL}\rangle = 0 \quad \textit{for all } k. \tag{13}$$

$|\mathscr{HL}\rangle$ is a BCS function [5, Eq. (6.66)]. The four terms of Eq. (11) are determinants. $\hat{K}|\ \rangle$ describes two holes (doubly-charged positive ion). $|\mathbf{1\bar{1}}\rangle$ is the particle-hole vacuum:

$$|\mathbf{1\bar{1}}\rangle = \hat{a}_1^+\hat{a}_{\bar{1}}^+\hat{K}|\ \rangle. \tag{14}$$

$|\mathbf{2\bar{2}}\rangle$ is a two-particle, two-hole excited state:

$$|\mathbf{2\bar{2}}\rangle = \hat{a}_2^+\hat{a}_{\bar{2}}^+\hat{a}_{\bar{1}}\hat{a}_1|\mathbf{1\bar{1}}\rangle. \tag{15}$$

$|\mathbf{1\bar{1}2\bar{2}}\rangle$ describes two particles (doubly-charged negative ion):

$$|\mathbf{1\bar{1}2\bar{2}}\rangle = \hat{\boldsymbol{a}}_2^+ \hat{\boldsymbol{a}}_{\bar{2}}^+ |\mathbf{1\bar{1}}\rangle. \tag{16}$$

$|\mathrm{HL}\rangle$ is the ground state *HL wave function.*

$$|\mathrm{HL}\rangle = \left[\frac{1}{u_1^4 + v_1^4}\right]^{1/2} (v_1^2 |\mathbf{1\bar{1}}\rangle - u_1^2 |\mathbf{2\bar{2}}\rangle \tag{17}$$

$$\equiv \left[\frac{1}{2(1+S^2)}\right]^{1/2} (|\chi_l \chi_{\bar{r}}\rangle + |\chi_r \chi_{\bar{l}}\rangle). \tag{18}$$

$|\chi_l \chi_{\bar{r}}\rangle$ and $|\chi_r \chi_{\bar{l}}\rangle$ describe overlapping orbitals outside a model core.

2.1.2. Unperturbed excited states. Normalized unperturbed excited states are HL quasiparticles or unpaired particles or holes above the vacuum.

$$\hat{\boldsymbol{\alpha}}_{a_1}^+ \hat{\boldsymbol{\alpha}}_{a_2}^+ \cdots \hat{\boldsymbol{\alpha}}_{a_n}^+ \hat{\boldsymbol{\alpha}}_{k_1}^+ \hat{\boldsymbol{\alpha}}_{k_2}^+ \cdots \hat{\boldsymbol{\alpha}}_{k_n}^+ |\mathscr{HL}\rangle. \tag{19}$$

$a(k)$ is restricted to particle (hole) labels of the particle-hole vacuum $|\mathbf{1\bar{1}}\rangle$. This ensures one-to-one correspondence with excited states of the particle-hole problem [7, Sect. 7.4.5]. Excited states with manifestly incorrect particle-number are excluded.

Side conditions are needed to enforce particle-number symmetry for some of the excited states. In particular, particle-number conservation is violated whenever at least one $k_i = 1$ or at least one $a_i = 2$ in Eq. (19). Some of this error is corrected by using the model Hamiltonian for the ground state ($\tilde{\boldsymbol{H}}_{\mathrm{HL}}$ in Sect. 2.2 below) in all calculations. This has been discussed for the special case of chemical potential [5, Sect. 6.3.4(i)]. The numerical studies reported in Part III show that such usage of $\boldsymbol{H}_{\mathrm{HL}}$ is commensurate with the accuracy of finite basis sets.

Other restrictions on unperturbed excited states are needed to avoid diagrammatic overcount. No part of the HL correlation energy may be counted by perturbative corrections. *Excited states with labels* $a_i = 2$ and $k_i = 1$ $\forall i = 1, \ldots, n$ *are not allowed.* This eliminates spurious states.

2.1.3. Occupation numbers and pairing numbers. ϕ_1 and ϕ_2 are fractionally occupied in $|\mathscr{HL}\rangle$ and $|\mathrm{HL}\rangle$. Occupation numbers (h_i) and pairing numbers (χ_i) for $|\mathscr{HL}\rangle$ may be compared to occupation numbers (n_i) and products of mixing coefficients (I_{12}) for $|\mathrm{HL}\rangle$. All may be expressed in terms of HLBV transformation coefficients:

$$\left.\begin{aligned} n_1 &= \frac{v_1^4}{u_1^4 + v_1^4} = n_{\bar{1}} \\ n_2 &= \frac{u_1^4}{u_1^4 + v_1^4} = n_{\bar{2}} \\ I_{12} &= -\frac{u_1^2 v_1^2}{u_1^4 + v_1^4} \end{aligned}\right\} \tag{20}$$

$$\left.\begin{aligned} h_i &= v_i^2 = h_{\bar{i}} \\ \chi_1 = \sqrt{h_1(1-h_1)} &= -\chi_{\bar{1}} = -\chi_2 = \chi_{\bar{2}} \end{aligned}\right\}. \tag{21}$$

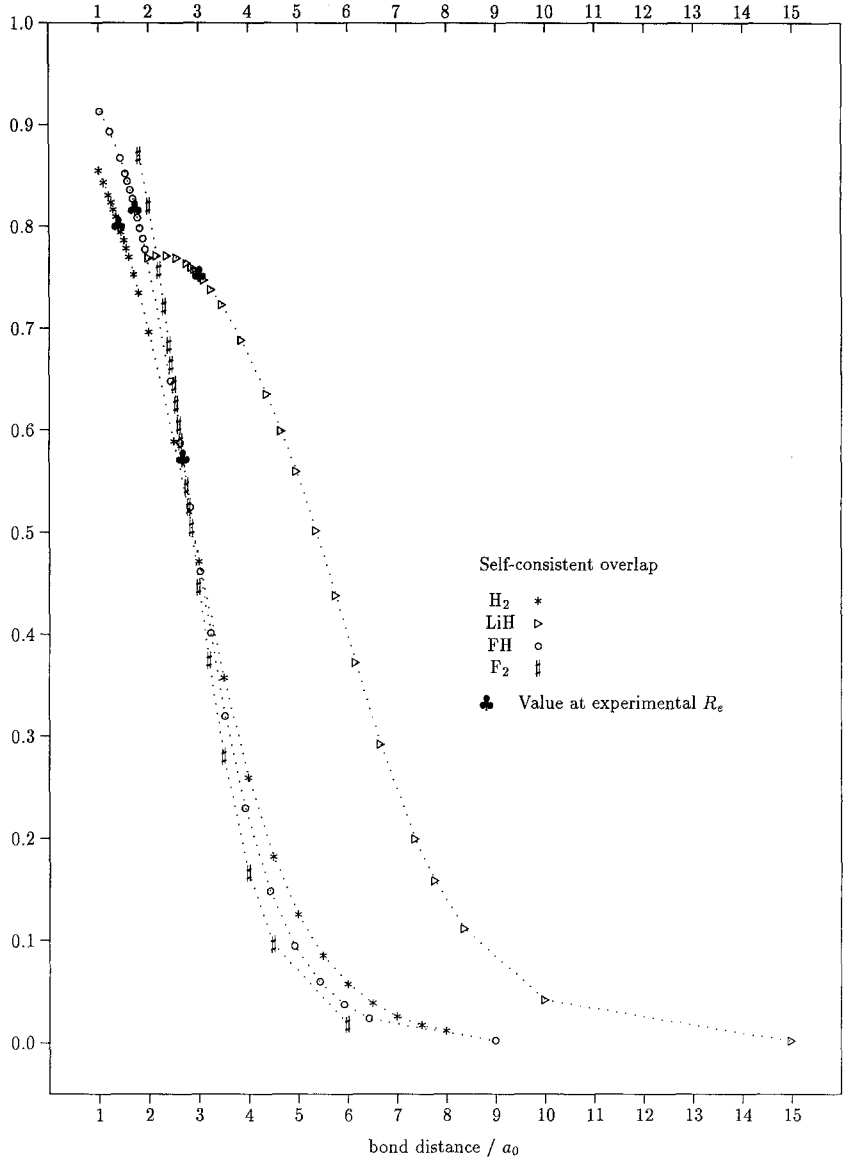

Fig. 1. Self-consistent overlap

h_i (χ_i^2) is a linear function of $S(S^2)$.

$$S = 2h_1 - 1 = 1 - 2h_2, \quad \chi_i^2 = \tfrac{1}{4}(1 - S^2). \tag{22}$$

$S(R)$ is plotted in Fig. 1. Curves for covalent bonds differ from weakly covalent LiH. $S(R_e)$ for F_2 is smaller than others because the bond is "long". $S(R_e)$ for LiH is large because metallic functions are large.

Occupation numbers (pairing numbers) are plotted in Fig. 2 (Fig. 3). Shapes of occupation-number curves in Hilbert space differ from those in Fock space.

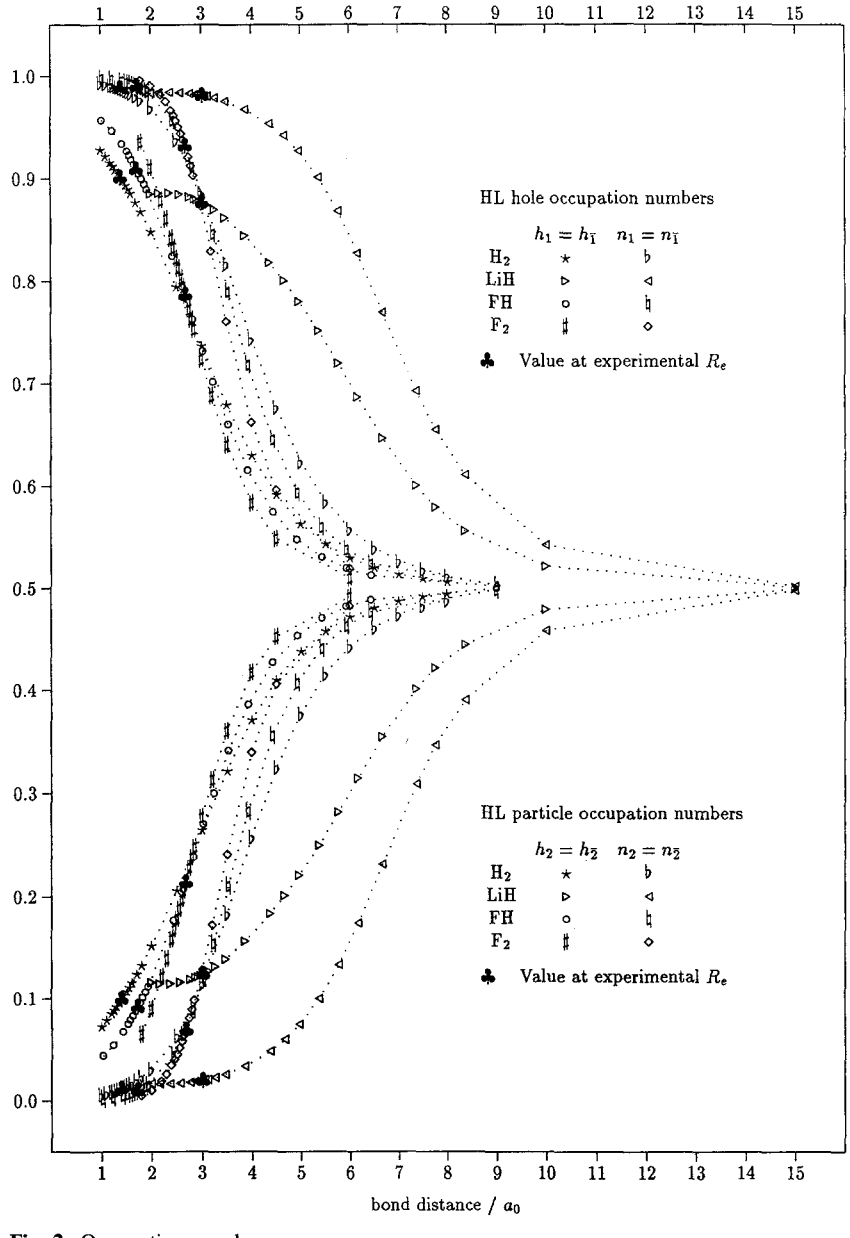

Fig. 2. Occupation numbers

All approach $\pm\frac{1}{2}$ at long bond distances. Occupation numbers for ϕ_1 (ϕ_2) in Fock space are smaller (larger) than in Hilbert space. Pairing numbers have larger magnitudes than I_{12}. Paired orbitals are always fractionally occupied. This is not predicted by the ordinary BCS saddle-point-type approximation: Near R_e, Hartree–Fock (HF) energies may lie below BCS saddle-point-type energies [8, 9]. Values at R_e for LiH are comparable to others. Smaller (larger) hole

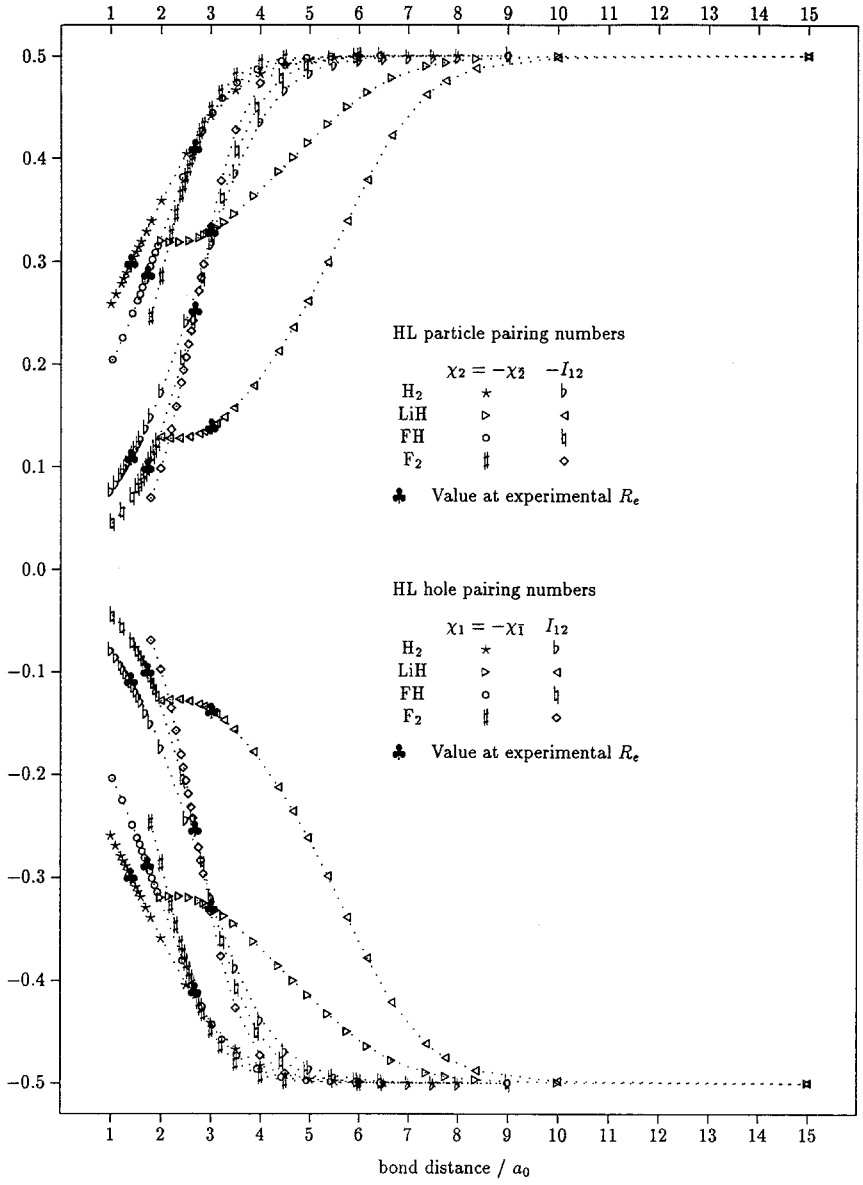

Fig. 3. Pairing numbers

(particle) occupation numbers and larger hole-particle pairing magnitudes are associated with the "long" covalent F_2 bond.

When $h_1 = h_{\bar{1}} = h_2 = h_{\bar{2}} = \frac{1}{2}$, $\hat{\alpha}_1\hat{\alpha}_{\bar{1}}$ and $\hat{\alpha}_2\hat{\alpha}_{\bar{2}}$ each describe one electron. The magnitude of the pairing number is maximal ($|\chi_i| = \frac{1}{2}$ for $i = 1, 2$). *Maximal pairing distributes bonding electrons equally on each atom.*

2.2. *Lipkin–Nogami Hamiltonian for the* HL *model*

$|\mathscr{H}\mathscr{L}\rangle$ does not conserve particle-number. A Lipkin–Nogami Hamiltonian can enforce particle-number symmetry [6]. It may be expanded about the correct average number of particles (two).

$$\left.\begin{aligned} \tilde{\boldsymbol{H}}_{HL} &= \hat{\boldsymbol{H}} - \hat{L}_{HL}^{[PN]} \\ \hat{L}_{HL}^{[PN]} &= \lambda_{1,HL}^{[PN]}(\hat{N}_{HL} - 2) + \tfrac{1}{2}\lambda_{2,HL}^{[PN]}(\hat{N}_{HL} - 2)^2 \end{aligned}\right\}. \tag{23}$$

$\hat{\boldsymbol{H}}$ is the ordinary Hamiltonian and $\hat{L}_{HL}^{[PN]}$ is an operator which enforces particle-number symmetry (L operator). $\lambda_{1,HL}^{[PN]}$ and $\lambda_{2,HL}^{[PN]}$ are basic parameters. $[PN]$ indicates particle-number conservation is enforced. $\hat{N}_{HL}$ is the HL number operator.

$$\hat{N}_{HL} = \sum_{k=\bar{2}}^{2} \hat{\boldsymbol{a}}_k^+ \hat{\boldsymbol{a}}_k. \tag{24}$$

2.2.1. HL *parameters.* With correct parameters, the Schrödinger equation for $|\mathrm{HL}\rangle$ and $\hat{\boldsymbol{H}}$ may be replaced by the Schrödinger equation for $|\mathscr{H}\mathscr{L}\rangle$ and $\tilde{\boldsymbol{H}}_{HL}$. Values are determined by side conditions [1, 6].

$$\lambda_{1,HL}^{[PN]} = \tfrac{1}{4}(\langle \mathbf{1\bar{1}2\bar{2}}|\hat{\boldsymbol{H}}|\mathbf{1\bar{1}2\bar{2}}\rangle - \langle|\hat{\boldsymbol{K}}^\dagger\hat{\boldsymbol{H}}\hat{\boldsymbol{K}}|\rangle) \tag{25}$$

$$\lambda_{2,HL}^{[PN]} = \tfrac{1}{4}(\langle \mathbf{1\bar{1}2\bar{2}}|\hat{\boldsymbol{H}}|\mathbf{1\bar{1}2\bar{2}}\rangle + \langle|\hat{\boldsymbol{K}}^\dagger\hat{\boldsymbol{H}}\hat{\boldsymbol{K}}|\rangle - 2\langle \mathrm{HL}|\hat{\boldsymbol{H}}|\mathrm{HL}\rangle). \tag{26}$$

$\langle \mathrm{HL}|\hat{\boldsymbol{H}}|\mathrm{HL}\rangle$ is the ground-state HL energy (first-order energy).

$$\langle \mathrm{HL}|\hat{\boldsymbol{H}}|\mathrm{HL}\rangle = \langle \mathscr{H}\mathscr{L}|\tilde{\boldsymbol{H}}_{HL}|\mathscr{H}\mathscr{L}\rangle = E_{HL} = E^{(1)}. \tag{27}$$

$\langle \mathbf{1\bar{1}2\bar{2}}|\hat{\boldsymbol{H}}|\mathbf{1\bar{1}2\bar{2}}\rangle$ and $\langle|\hat{\boldsymbol{K}}^\dagger\hat{\boldsymbol{H}}\hat{\boldsymbol{K}}|\rangle$ are single-determinant energies of systems with total charge equal two. In the molecular regime, $\langle \mathbf{1\bar{1}2\bar{2}}|\hat{\boldsymbol{H}}|\mathbf{1\bar{1}2\bar{2}}\rangle$ ($\langle|\hat{\boldsymbol{K}}^\dagger\hat{\boldsymbol{H}}\hat{\boldsymbol{K}}|\rangle$) is the energy of a doubly charged negative (positive) molecular ion calculated with orbitals for the neutral molecule. In the atomic regime, $\langle \mathbf{1\bar{1}2\bar{2}}|\hat{\boldsymbol{H}}|\mathbf{1\bar{1}2\bar{2}}\rangle$ ($\langle|\hat{\boldsymbol{K}}^\dagger\hat{\boldsymbol{H}}\hat{\boldsymbol{K}}|\rangle$) is the energy of two singly-charged negative (positive) atomic ions calculated with orbitals for neutral atoms. Negative ions may be unstable in all regimes [10, 11].

$\lambda_{2,HL}^{[PN]}$ is a finite-difference approximation that replaces $\partial^2/\partial N^2 \times [\langle \mathscr{H}\mathscr{L}|\hat{\boldsymbol{H}}|\mathscr{H}\mathscr{L}\rangle]$ by the average of model energies for creating two holes and two particles. Averages are expected to be positive and to become large at small bond distances. Similar behavior is expected from similar types of bonds. Limiting values at long bond distances are determined by atomic states. If energy levels of HL quasiparticles were continuous, $\lambda_{2,HL}^{[PN]}$ would vanish identically.

$\lambda_{1,HL}^{[PN]}$ is the average of the energy-difference between excited states with two holes and two particles. An estimate is:

$$\lambda_{1,HL}^{[PN]} \sim \frac{\epsilon_1 + \epsilon_2}{2} \tag{28}$$

where ϵ's are orbital energies for a neutral determinant. Equation (28) is usually negative; however, repulsions between doubly occupied ϕ_1 and ϕ_2 in the model of the negative ion dominate at short bond distances and cause Eq. (28) to become positive. Limiting values at long bond distances are determined by atomic states. If energy-levels of HL quasiparticles were continuous, $\lambda_{1,HL}^{[PN]}$ would be analogous to chemical potential.

Effective parameters. Second-quantized models identify effective parameters by *normal ordering of operators*. Normal ordering with respect to $|\mathscr{HL}\rangle$ is a special case of normal ordering for the BCS function [12, Sect. 11.4]. It is denoted by $:\cdots:$, where $\cdots$ stands for a product of second-quantized operators.

Normal ordering of $\hat{L}_{HL}^{[PN]}$ yields a sum of zero- ($\lambda_{0,HL}^{[PN]}$), one- ($\hat{L}_{HL,1}^{[PN]}$), and two-body ($\hat{L}_{HL,2}^{[PN]}$) L operators [3].

$$\hat{L}_{HL}^{[PN]} = \hat{L}_{HL,2}^{[PN]} + \hat{L}_{HL,1}^{[PN]} + \lambda_{0,HL}^{[PN]}. \tag{29}$$

Those needed to enforce particle-number symmetry may be defined with the canonical representation [1]:

$$\hat{L}_{HL,2}^{[PN]} = \tfrac{1}{2}\lambda_{2,HL}^{[PN]} :\hat{N}_{HL}^2: \tag{30}$$

$$\hat{L}_{HL,1}^{[PN]} = \left\{ \begin{array}{l} \lambda_{HL}^{[PN]} :\hat{N}_{HL}: - \lambda_{2,HL}^{[PN]} \sum_{k=\bar{2}}^{2} h_k :\hat{a}_k^+ \hat{a}_k: \\ + \lambda_{2,HL}^{[PN]} \sum_{k=\bar{2}}^{2} \chi_k (:\hat{a}_{\bar{k}}\hat{a}_k: + :\hat{a}_k^+ \hat{a}_{\bar{k}}^+ :) \end{array} \right\} \tag{31}$$

$$\lambda_{HL}^{[PN]} = \lambda_{1,HL}^{[PN]} + \tfrac{1}{2}\lambda_{2,HL}^{[PN]} \tag{32}$$

$$\lambda_{0,HL}^{[PN]} = 4\chi_1^2 \lambda_{2,HL}^{[PN]}. \tag{33}$$

They satisfy several inequalities:

$$\left. \begin{array}{c} \lambda_{2,HL}^{[PN]} > \lambda_{HL}^{[PN]} > \lambda_{1,HL}^{[PN]} \\ \lambda_{2,HL}^{[PN]} \geqslant \lambda_{0,HL}^{[PN]} \end{array} \right\}. \tag{34}$$

$\lambda_{HL}^{[PN]}$ is a finite-difference approximation to $\partial/\partial N[\langle \mathscr{HL}|\hat{\boldsymbol{H}}|\mathscr{HL}\rangle]$, with all other variables held constant. If energy levels were continuous, the finite-difference would equal the derivative, and $\lambda_{HL}^{[PN]}$ would be analogous to chemical potential. Like chemical potential for ordinary BCS theory, $\lambda_{HL}^{[PN]}$ satisfies a gap equation. Gap equations and Eq. (32) give the same answer [1].

$\lambda_{0,HL}^{[PN]}$ is the difference between ground-state averages of the Hamiltonian:

$$\lambda_{0,HL}^{[PN]} = \langle \mathscr{HL}|\hat{\boldsymbol{H}}|\mathscr{HL}\rangle - \langle \mathrm{HL}|\hat{\boldsymbol{H}}|\mathrm{HL}\rangle > 0. \tag{35}$$

All other parameters involve derivatives of $\lambda_{0,HL}^{[PN]}$ with respect to particle-number:

$$\left. \begin{array}{c} \dfrac{\partial^k}{\partial N^k}[\lambda_{0,HL}^{[PN]}] = \dfrac{\partial^k}{\partial N^k}[\langle \mathscr{HL}|\hat{\boldsymbol{H}}|\mathscr{HL}\rangle] \\ \lambda_{2,HL}^{[PN]} = \dfrac{\partial^2}{\partial N^2}[\lambda_{0,HL}^{[PN]}] \\ \lambda_{HL}^{[PN]} = \dfrac{\partial}{\partial N}[\lambda_{0,HL}^{[PN]}] \\ \lambda_{1,HL}^{[PN]} = \left(\dfrac{\partial}{\partial N} + \dfrac{1}{2}\dfrac{\partial^2}{\partial N^2}\right)[\lambda_{0,HL}^{[PN]}] \end{array} \right\}. \tag{36}$$

They are expected to vary more rapidly than $\lambda_{0,HL}^{[PN]}$ in the molecular region.

Parameters are plotted in Fig. 4. There are three curves for each molecule at long bond distances:

$$\lambda_{2,HL}^{[PN]} = \lambda_{0,HL}^{[PN]} > \lambda_{HL}^{[PN]} > \lambda_{1,HL}^{[PN]}, \quad \text{for } R \to \infty. \tag{37}$$

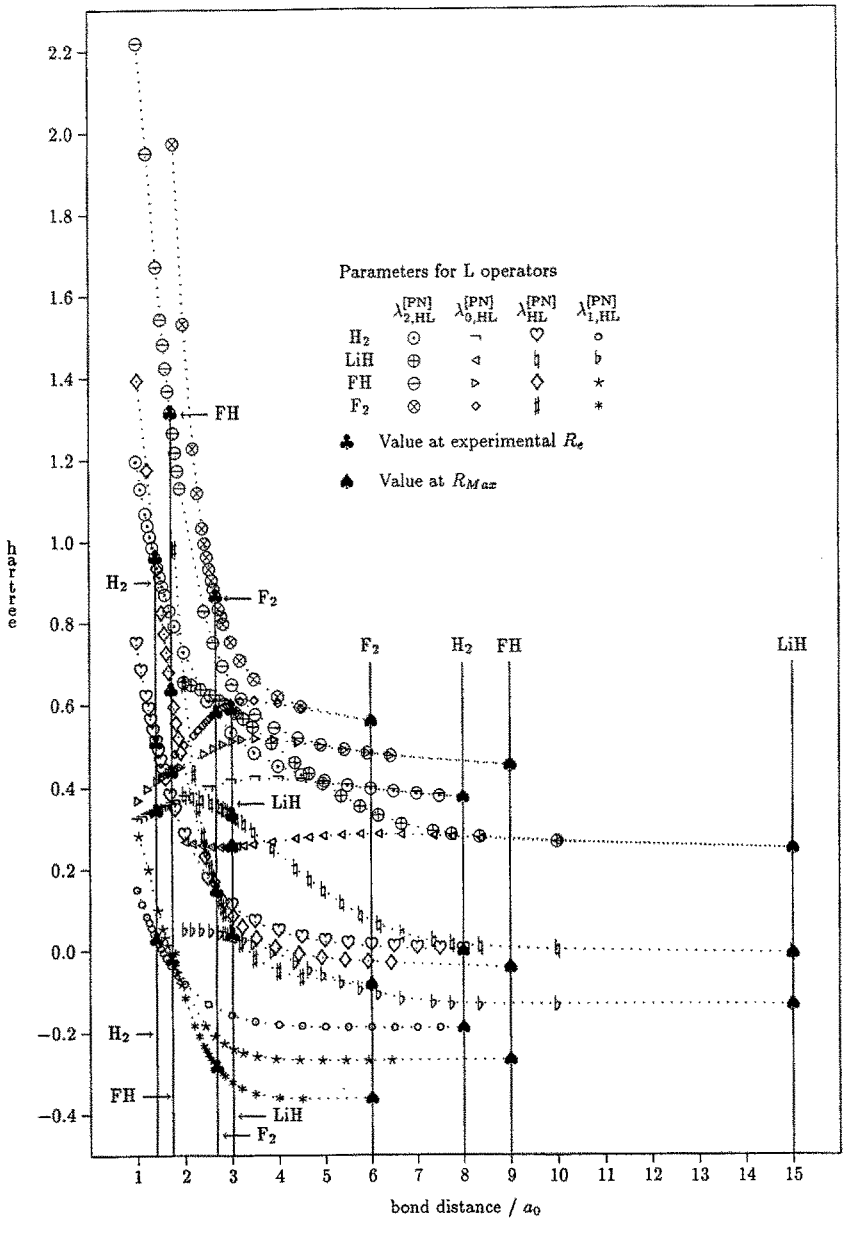

Fig. 4. Parameters for L operators

Orderings for the "long" F_2 bond differ from others at R_e:

$$\left.\begin{array}{ll} \lambda^{[PN]}_{2,HL} > \lambda^{[PN]}_{0,HL} > \lambda^{[PN]}_{HL} > \lambda^{[PN]}_{1,HL}, & \text{for } F_2 \text{ at } R_e \\ \lambda^{[PN]}_{2,HL} > \lambda^{[PN]}_{HL} > \lambda^{[PN]}_{0,HL} > \lambda^{[PN]}_{1,HL}, & \text{for all others at } R_e \end{array}\right\}. \tag{38}$$

Slopes of $\lambda^{[PN]}_{0,HL}$ are positive at R_e. Slopes of its derivatives with respect to particle-number are negative at R_e.

2.2.2. Unperturbed Hamiltonian. One-body terms of the model Hamiltonian are identified by the normally ordered expansion of $\tilde{H}_{HL}$ is the canonical representation [3]. The unperturbed Hamiltonian $\tilde{K}_{\mathscr{H}\mathscr{L},1}$ is the sum of diagonal elements of the one-body Hamiltonian after the HLBV transformation.

$$\left.\begin{aligned} \tilde{K}_{\mathscr{H}\mathscr{L},1} &= \sum_q \kappa_{qq} \hat{\alpha}_q^+ \hat{\alpha}_q \\ \kappa_{11} = \sqrt{v_{11}^2 + \mu_{11}^2}, \quad \kappa_{22} &= \sqrt{v_{22}^2 + \mu_{22}^2} \\ \kappa_{qq} = -v_{qq}, \quad \text{holes}; \quad \kappa_{qq} &= v_{qq}, \quad \text{particles} \end{aligned}\right\}. \tag{39}$$

$v(\mu)$ is the self-consistent energy (self-consistent pairing potential). Diagonalization of v defines canonical holes and particles for BCSLN–HL. *Equation* (39) *is subject to the condition that v is diagonalized in the hole and particle subspaces.*

3. BCSLN–HL (2 and 3)

The perturbation $\tilde{V}^{(1)}_{\mathscr{H}\mathscr{L},2}$ is the two-body operator in the canonical representation:

$$\tilde{V}^{(1)}_{\mathscr{H}\mathscr{L},2} = \frac{1}{2} \sum_{ijkl} V^{(1)}_{ijkl} : \hat{a}_i^+ \hat{a}_j^+ \hat{a}_l \hat{a}_k : \tag{40}$$

$V^{(1)}_{ijkl}$ is the difference between matrix elements for the electron-electron repulsion and the two-body L operator [3]. Perturbative corrections are represented by an exact order-by-order series expansion of non-redundant FD. Up to any order, the sum of all diagrams scales correctly against extensive parameters of the system.

FD are evaluated for the special representation $\hat{\alpha}$ [1]. Non-bubble diagrams are calculated with general formulae [3]. Energy denominators are products of sums of κ_{qq}. Renormalization adds a term to $V^{(1)}_{ijkl}$ and modifies κ_{qr}, $q \neq r$. The latter are bubble elements. Renormalization and general formulae for bubble diagrams are reported elsewhere [1, 13].

3.1. Diagrammatic overcount

A convenient expression for energy up to order N is:

$$E^{(N)} = W^{(N)}_{HL} + \delta D^{(K)}, \quad \delta D^{(K)} = \sum_{K=2}^{N} D^{(K)}. \tag{41}$$

$D^{(K)}$ is the sum of all non-bubble FD of order K [3]. *Normal HL energy* $W^{(N)}_{HL}$ is E_{HL} with all FD for HL quasiparticles removed up to Nth order:

$$W^{(N)}_{HL} = E_{HL} - \delta M^{(N)}_{HL}. \tag{42}$$

$\delta M^{(N)}_{HL}$ is the sum of *model-included FD* for HL quasiparticles up to order N:

$$\delta M^{(N)}_{HL} = \delta D^{(N)}_{HL} + \delta B^{(N)}_{HL}, \quad \left.\begin{aligned} \delta D^{(N)}_{HL} &= \sum_{K=2}^{N} D^{(K)}_{HL} \\ \delta B^{(N)}_{HL} &= \sum_{K=2}^{N} B^{(K)}_{HL} \end{aligned}\right\}. \tag{43}$$

$\delta M_{HL}^{(N)}$ is counted by E_{HL} and $\delta D^{(K)}$. Using $W_{HL}^{(N)}$ instead of E_{HL} in Eq. (41) avoids diagrammatic overcount up to Nth order.

The two pieces of $\delta M_{HL}^{(N)}$ correspond to interactions counted explicitly and implicitly by renormalized FD. The explicit term ($\delta D_{HL}^{(N)}$) accounts for Nth order *HL quasiparticle scattering diagrams*. HL quasiparticle scattering diagrams range over all non-bubble diagrams whose down-arrows (up-arrows) are labelled exclusively by HL quasiparticle label 1 (2). All spins are included.

The implicit term ($\delta B_{HL}^{(N)}$) is the sum of all Nth order *dangerous HL bubble diagrams*. It removes redundant pieces of HL self-energy from renormalized diagrams. All bubble diagrams are dangerous. *Safe* bubble diagrams vanish because v is diagonalized in the hole and particle subspaces.

Model-included FDs are plotted in Figs. 5 (second order) and 6 (third order). Signs of $D_{HL}^{(K)}$ and $M_{HL}^{(K)}$ oscillate. $B_{HL}^{(K)}$ are always negative.

$$\left.\begin{aligned} B_{HL}^{(2)} = \delta B_{HL}^{(2)} > D_{HL}^{(2)} = \delta D_{HL}^{(2)} > M_{HL}^{(2)} = \delta M_{HL}^{(2)} \\ B_{HL}^{(3)} < M_{HL}^{(3)} < D_{HL}^{(3)} \\ \delta D_{HL}^{(3)} > \delta B_{HL}^{(3)} > \delta M_{HL}^{(3)} \end{aligned}\right\}. \tag{44}$$

Model FD vanish where distances between paired electrons are large. Except for $\delta B_{HL}^{(3)}$ for H_2, all curves exhibit minima. Those for the "long" F_2-bond are on opposite sides of R_e relative to all others.

The $\delta M_{HL}^{(N)}$ and other model FD are computed with renormalized one- and two-electron matrix elements. Thus, $W_{HL}^{(N)}$ is a *renormalized* energy which adiabatically connects "uncorrelated" molecular energies to correct atomic energies. Renormalization sums divergent FD for the HF model to all orders. Up to order N, perturbative corrections to $W_{HL}^{(N)}$ and E_{HF} are in one-to-one correspondence. When the HF model is a correct starting model, $E_{HL} \sim W_{HL}^{(N)} \sim E_{HF}$. At large bond distances, $W_{\mathrm{HL}}^{(N)} = E_{\mathrm{HF}}(atom\ l) + E_{\mathrm{HF}}(atom\ r) = E_{\mathrm{HL}}$.

3.2. *Analysis of perturbative corrections*

It is convenient to rewrite Eq. (41) as:

$$\left.\begin{aligned} E^{(N)} &= E_{HL} + \delta E^{(N)} \\ \delta E^{(N)} &= \sum_{K=2}^{N} \delta^{(K)} E \end{aligned}\right\}. \tag{45}$$

$\delta E^{(N)}$ is the total perturbative correction up to order N. $\delta^{(K)}E$ is the Kth-order perturbative correction.

$$\delta^{(K)}E = D^{(K)} - M_{HL}^{(K)}. \tag{46}$$

Scaled perturbative corrections are plotted in Fig. 7.

$$\delta^{(K)}\bar{E} = \frac{\delta^{(K)}E}{N_{elec}}. \tag{47}$$

N_{elec} is the number of electrons for the molecule. $\delta^{(2)}\bar{E}$ range from about -0.008 hartree for H_2 to about -0.025 hartree for F_2 and FH. For comparison, $\delta\bar{E}^{(\infty)} \approx -0.04$ hartree for the electron gas [14, Table 3-8], and $\delta^{(2)}\bar{E} \approx -0.02$ hartree for the lowest-lying open-shell states of CaO [15]. $\delta^{(3)}\bar{E}$ are an order of

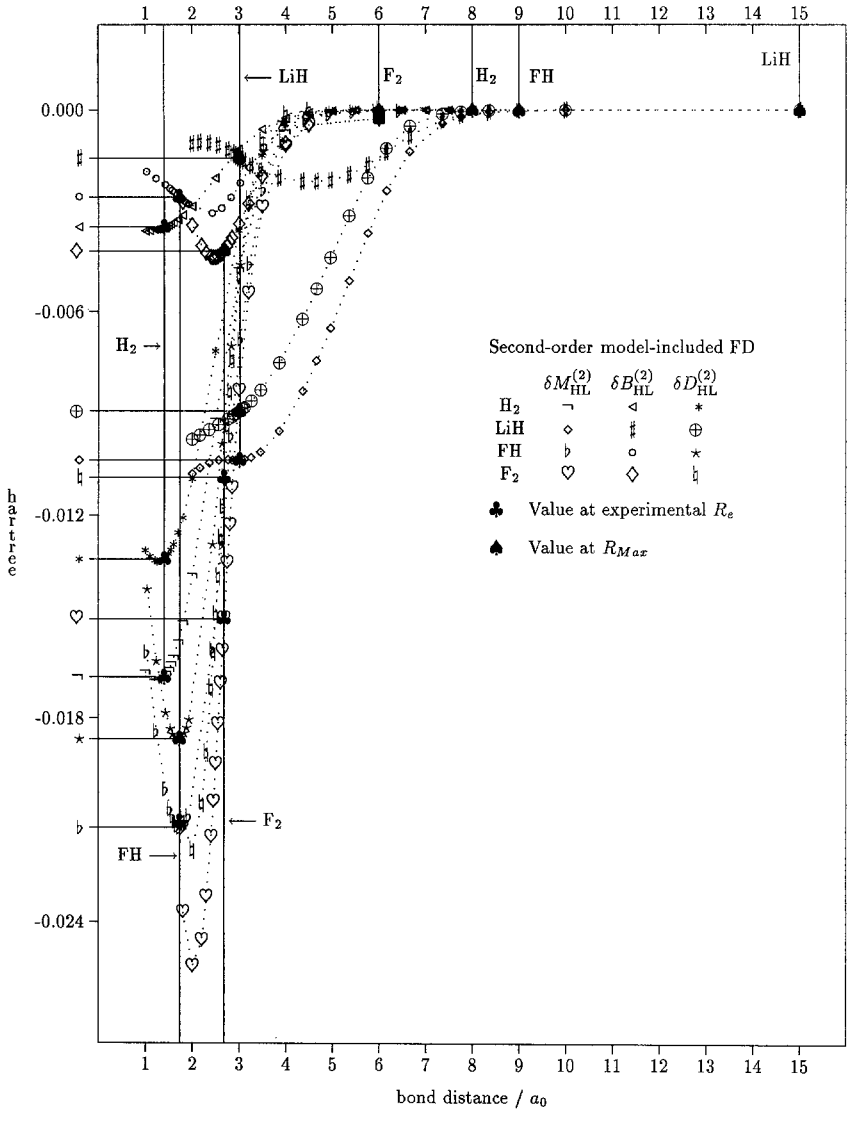

Fig. 5. Second-order HL model-included FD

magnitude smaller than $\delta^{(2)}\bar{E}$, and are sometimes positive and sometimes negative. At long bond distances, all curves are nearly constant and essentially describe atomic correlation. $\delta^{(K)}\bar{E}$ for LiH are more nearly constant than others, apparently because LiH is weakly covalent. $\delta^{(2)}\bar{E}$ for F_2 and FH are similar. $\delta^{(2)}\bar{E}$ for FH appear 10% smaller at long bond distances: This disappears if $N_{elec} = 9$ is used for FH. $\delta^{(3)}\bar{E}$ for F_2 and FH are almost indistinguishable in Fig. 7.

$\delta^{(N)}\bar{E}$ for H_2 do not vanish at long bond distances: This is because side conditions for unperturbed excited states are neglected (see Sect. 3.1 of Paper III of this series).

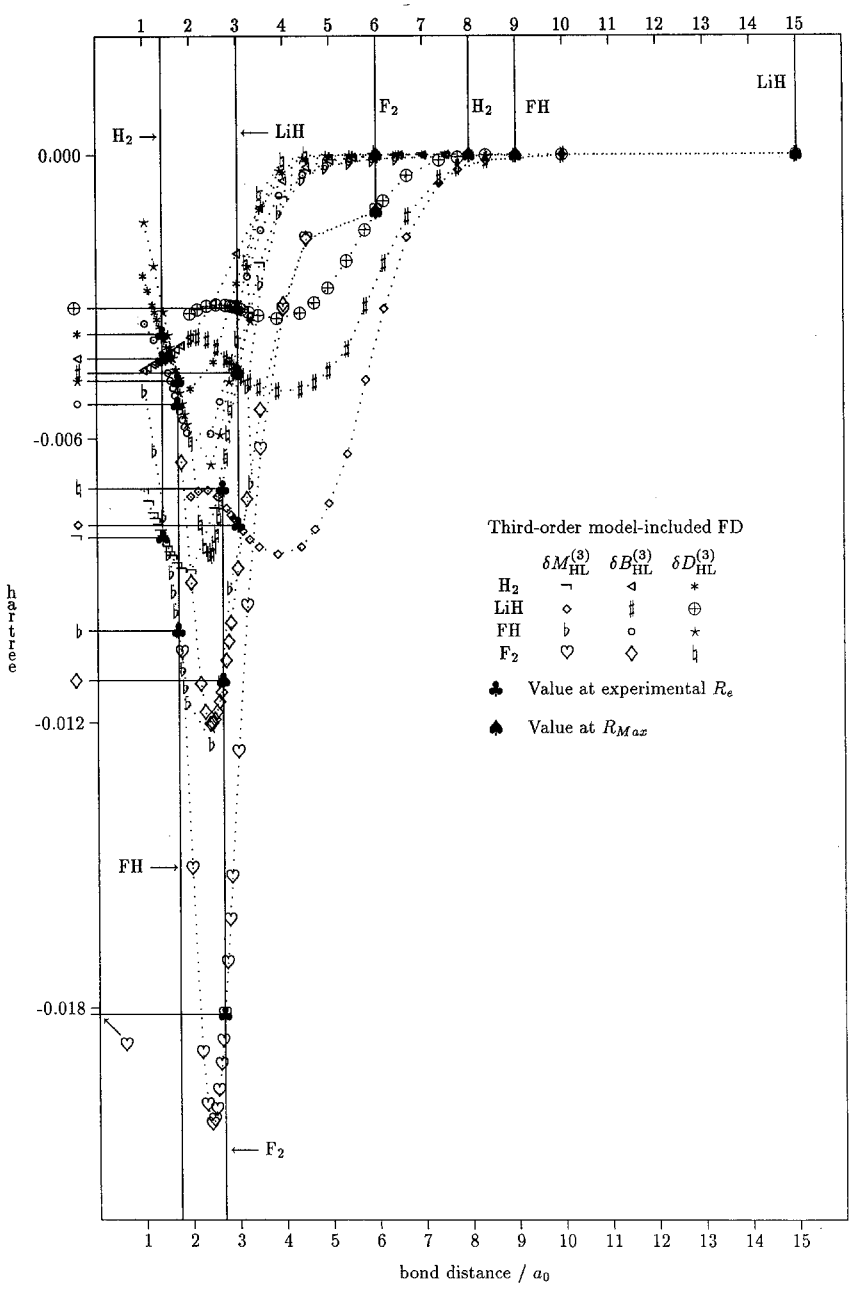

Fig. 6. Third-order HL model-included FD

$\delta^{(3)}E/\delta^{(2)}E$ are plotted in Fig. 8. Except for H_2, magnitudes are similar. Positive (negative) ratios correspond to monotonic (oscillatory) convergence. Convergence for H_2 and LiH (F_2 and FH) is monotonic (oscillatory) near R_e. In the molecular regime, BCSLN–HL(1) starting models – the *Ansatz* plus the

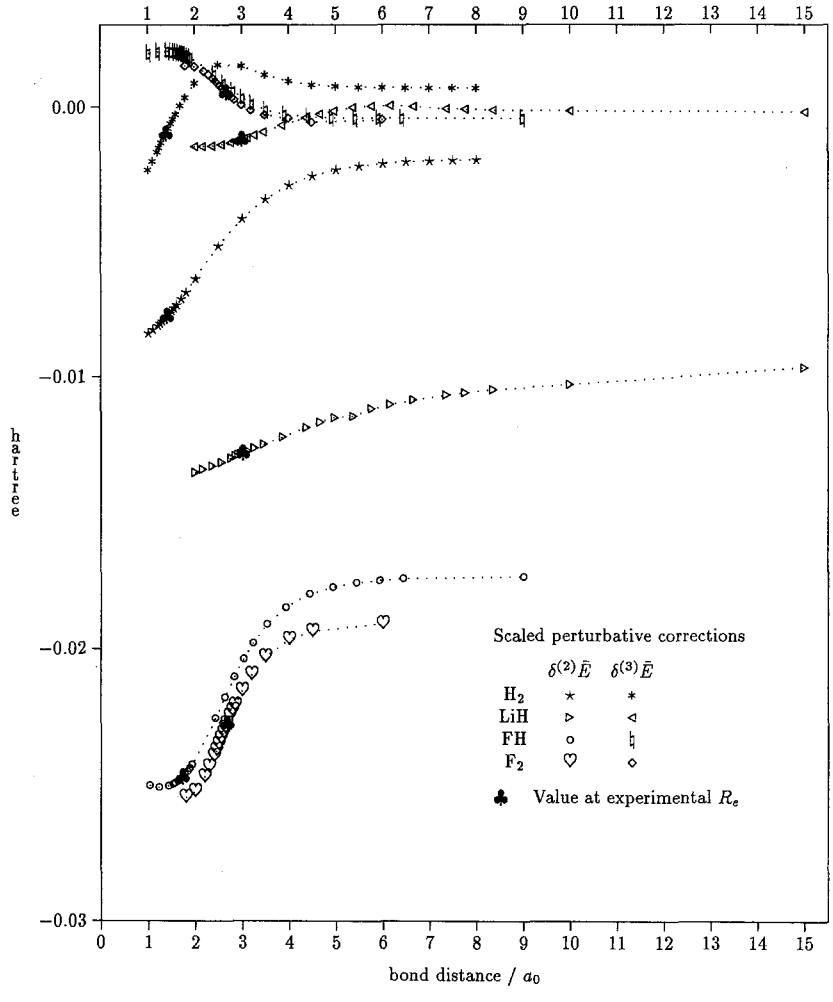

Fig. 7. Scaled perturbative corrections

basis sets – for H_2 and LiH are more accurate than for F_2 and FH. In the atomic regime, BCSLN–HL(1) appears to be a comparable starting point for all systems.

$\delta^{(K)}E/E_{HL}$ are also plotted in Fig. 8. Largest magnitudes and variations are about 2%. Curves for F_2 and FH are indistinguishable.

4. Conclusions

Magnitudes of successive perturbative corrections through third order suggest that BCSLN–HL(N) converges. Third-order corrections are about an order of magnitude smaller than second-order corrections. Total corrections through third order are about two orders of magnitude smaller than first-order energies.

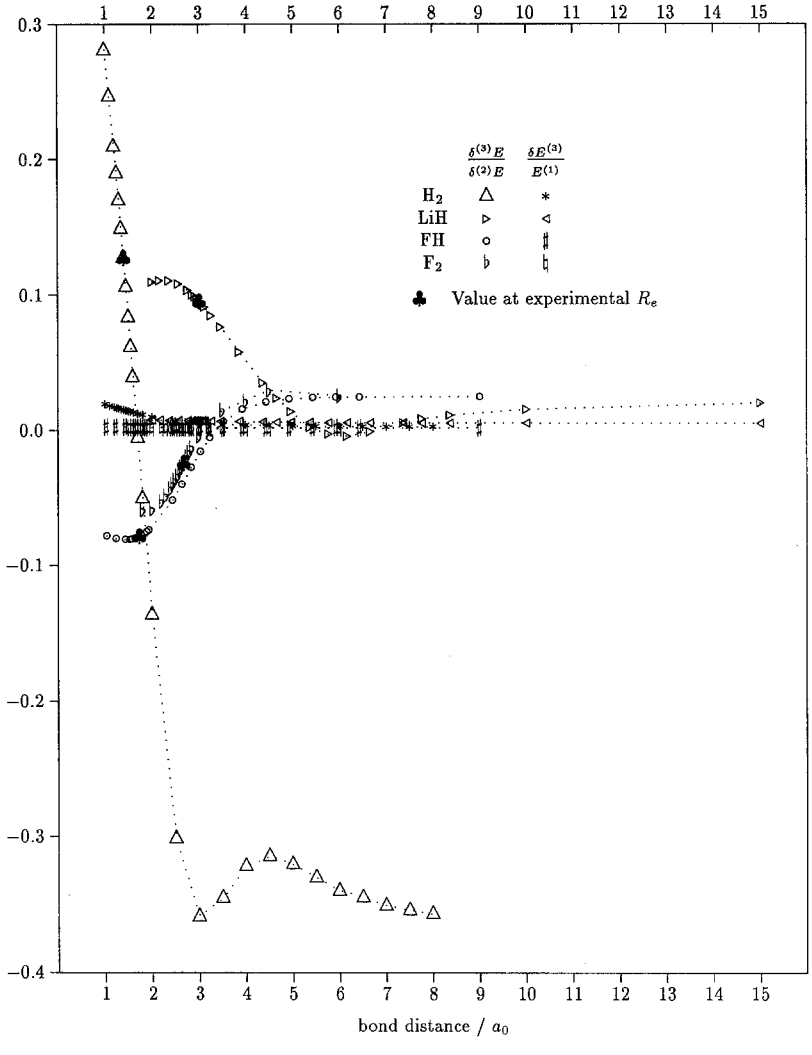

Fig. 8. Invariant ratios

Oscillating perturbative corrections near R_e for F_2 and FH indicate slower convergence. More extensive unperturbed BCSLN models for these molecules could be useful. Convergence in atomic regions is satisfactory.

Acknowledgments. Prof. W. C. Ermler and Dr. S. Wilson are thanked for software.

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