Effective electronic Hamiltonian for quantum subsystem in hybrid QM/MM methods as derived from APSLG description of electronic structure of classical part of molecular system[☆]

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Abstract

The general formulae representing separation of electronic variables of quantum (reactive) subsystem from those describing electrons in the classical (chemically inert) part of molecular system are specified for the case when the electronic structure of the latter is described by a semi-empirical method based on the trial wave function having the form of antisymmetrized product of strictly localized geminals (APSLG) which leads to a local description of molecular electronic structure in terms of bond functions and lone pair functions. This allowed us to give an explicit form of the effective electronic Hamiltonian for the quantum subsystem and also by this to sequentially derive the explicit form of the QM/MM junction between the quantum and classical subsystems. The latter turned out to be a sum of the contributions from different chemical bonds and lone pairs residing in the classical part of the system. Numerical estimates for the effect of the renormalization of the Coulomb interaction of π-electrons due to presence of σ-bonds are performed according to the derived formulae. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Electronic Hamiltonian; Semi-empirical method; Quantum subsystem

1. Introduction

At present research in chemistry and in related areas of science reached the state that requires constructing potential energy surfaces (PES) of large systems. This problem can be encountered in the context of chemical reactions of biomolecules, enzymatic reactions, surface reactions and reactions in condensed media. Applying methods of quantum mechanics (QM) to construct PESs in each point of the nuclear configuration space faces the problem of $O(N^m)$-scaling of the QM methods (N is the number

of one-electron states involved in the calculation). Practically the exponent m may reach values of 5–7 for high quality modern QM methods necessary to describe chemical reactivity (bond cleavage and bond formation), which restricts their applicability to molecular systems of rather small size [1]. However, the detailed QM description is necessary for the electronic structure of the reactive site only. The contribution of the rest of molecular system (i.e. of its chemically inert part) to the PES of the system can be calculated by molecular mechanics (MM), which has to reproduce only general features of this part of the molecular system. Thereby the hybrid quantum-mechanical/molecular mechanical (QM/MM) computational schemes become very popular (Refs. [2–8]). This approach significantly reduces

the computational costs of PES construction for large systems because only a small part of the latter is considered on the computationally expensive QM level.

There exist several QM/MM schemes implemented in a number of computation packages (see, for example, Refs. [2–8]). The diversity of such approaches is due to variety of both QM and MM methods combined and of the functional form of the junction between them. For example, in Ref. [2] the intersystem Coulomb and exchange integrals are represented as linear combinations of exponential functions with subsequent parametrization; in Refs. [3,4] "junction dummy atoms" are introduced; in Ref. [9] the interactions between subsystems are represented also by a sum of electrostatic and van der Waals interactions with adjusted parameters, etc. The common feature of all the mentioned approaches as well as of many others is that the form of the junction parametrized in each of them results from certain ad hoc postulate rather than from a sequential derivation. On the other hand, in Ref. [10] it was proposed to construct a consistent form of the QM/MM junction with use of an explicit procedure of separation of electronic variables. The latter is performed in Ref. [11] by using the Löwdin partition technique [12,13] and the group function (GF) formalism [14]. In Refs. [10,11], the expression for the effective Hamiltonian for the quantum (reactive) part of a molecular system has been obtained and the form of the QM/MM junction has been represented as a sum of operator averages over the implicit wave function of the classical (inert) subsystem, which is assumed to describe the electronic ground state of the latter. The present work is devoted to derivation of the explicit form of the effective Hamiltonian for the quantum system and, therefore, of the PES of the combined system and of the specific form of the QM/MM junction for a special local form of the wave function of the inert subsystem which has been constructed in Refs. [15,16] to ensure a ready transition to a description of the MM type which will be described elsewhere [17].

2. Effective Hamiltonian for quantum system

Now we briefly review the main notations and results of Ref. [11], where the general expression for

the effective Hamiltonian has been proposed. We denote two subsystems of the whole molecular system by indices R (reactive) and M (inert), where the R-subsystem is considered as a quantum one, whereas the M-subsystem must be finally treated on the classical (MM) level of approximation. The Hamiltonian for the whole system is a sum of Hamiltonians for the subsystems and of the operators for the interactions between the subsystems:

$$H = H^R(q) + H^M(q) + V^c(q) + V^r(q), \qquad (1)$$

where for the sake of simplicity only the Coulomb V^c and the resonance V^r (electron transfer) interactions are considered. Further, the Hamiltonian for the M-subsystem is subdivided into the Hamiltonian for the free (without reagents) M-subsystem H_0^M and the operator describing attraction of electrons of the M-subsystem to the cores of the R-subsystem $\mathcal{V}^R$. Analogous subdividing is performed for the R-subsystem. To justify usage of different levels of approximation to different parts of the whole system (specifically, of the MM-like scheme for the M-subsystem), the wavefunction for the whole system is represented by the antisymmetrized product of electronic wavefunction for the R-subsystem and that of the ground state for the free M-subsystem (i.e. of the ground state function of H_0^M):

$$\Psi_k = \Phi_k^R \wedge \Phi_{00}^M. \qquad (2)$$

The exact wavefunction of any electronic state of the whole system can be recast in the form:

$$\Psi_k = \sum_{n_M n_R} \sum_{i_M i_R} C_{i_M i_R}^k (n_M n_R) \Phi_{i_M 0}^M(n_M) \wedge \Phi_{i_R}^R(n_R), \qquad (3)$$

$(n_M + n_R = N_e)$.

The transition from the wavefunction of the general form Eq. (3) to the necessary form of Eq. (2) is made by performing two sequential Löwdin projection procedures: the first one to the subspace of the states with fixed number of electrons in the subsystems (projection operator P and its complementary projection operator $Q = 1 - P$) and the second one—to the states of the type Eq. (2), i.e. containing the ground state wavefunction of the free M-subsystem as the multiplier (projection operator $\mathcal{P}$ and its complementary projection operator $\mathcal{Q} = 1 - \mathcal{P}$). After the first

projection, we obtain

$$H_{\text{eff}}(q, E) = PH^R(q)P + PH^M(q)P + PV^c(q)P$$

$$+ PV^{\text{rr}}(q, E)P + \frac{e^2}{2} \sum_{\substack{A \neq B \\ A \in R, B \in M}} Z_A^R Z_B^M R_{AB}^{-1}, \qquad (4)$$

where

$$V^{\text{rr}}(q, E) = V^r(q)Q(E - QHQ)^{-1}QV^r(q)$$

$$= V^r(q)QR(q, E)QV^r(q). \qquad (5)$$

The second projection and subsequent averaging over the ground state of the M-subsystem give the effective Hamiltonian for the R-subsystem:

$$\mathscr{H}_{\text{eff}}^R(q, E, \omega) = H_0^R(q) + \delta V^M + \langle\langle PV^{\text{rr}}P \rangle\rangle_M$$

$$+ \langle \Phi_{00}^M | P\mathscr{V}^R P | \Phi_{00}^M \rangle$$

$$+ \langle \Phi_{00}^M | P\mathscr{W}(q, E)P \mathscr{2R}(\omega)\mathscr{2}P\mathscr{W}(q, E)P | \Phi_{00}^M \rangle$$

$$+ \frac{e^2}{2} \sum_{\substack{A \neq B \\ A \in R, B \in M}} Z_A^R Z_B^M R_{AB}^{-1}, \qquad (6)$$

where

$$\delta V^M = \mathscr{V}^M + \langle\langle PV^c P \rangle\rangle_M \approx 0 \qquad (7)$$

and

$$P\mathscr{W}P = PV^c P + PV^{\text{rr}}P + P\mathscr{V}^R P. \qquad (8)$$

The above general form of the effective Hamiltonian was obtained in Ref. [11]. In the present paper, we perform the averaging assuming that the wave-function of the M-subsystem has a specific form, which gives the local description of the latter.

The form of the wave function of the M-subsystem to be used to perform the averaging has to allow to represent the renormalization of Hamiltonian for the quantum subsystem as a sum of contributions from one or more chemical bonds or lone pairs. This is done to maintain consistency with the adopted MM type of description for the M-subsystem. For this purpose, we must use a quantum-chemical method, the energy of which can be presented in a MM-like form. The MM scheme assumes the transferability of the functions representing geometry dependence of different contributions to the molecular energy. Such

a transferability is shown to be achieved (Refs. [15,16]) for the trial wave function in the form of the antisymmetrized product of strictly localized orbitals (APSLG) [18]. The wave function of this method is constructed from two-electron functions (geminals) assigned to chemical bonds and lone pairs:

$$|\Phi\rangle = \prod_k g_k^+ |0\rangle, \qquad (9)$$

where

$$g_k^+ = u_k r_{k\alpha}^+ r_{k\beta}^+ + v_k l_{k\alpha}^+ l_{k\beta}^+ + w_k(r_{k\alpha}^+ l_{k\beta}^+ + l_{k\alpha}^+ r_{k\beta}^+),$$

$$(u_k^2 + 2w_k^2 + v_k^2 = 1) \qquad (10)$$

is the electronic pair creation operator for the kth geminal. Each of the orbitals r_k and l_k assigned to the kth chemical bond is a linear combination of the AO's centered on one atom only, i.e. a hybrid orbital (HO). The unitary matrices of transition from the AO basis to the HO basis and the geminal expansion coefficients u_k, v_k, and w_k are determined variationally in Refs. [15,16] for a wide range of organic molecules. For the purposes of the present paper, it is important to note that the energy of molecule in the APSLG approximation can be represented by a sum of inter-bond and intrabond (we use the term bond for usual chemical bonds and lone pairs) contributions and that the parameters of these contributions are well transferable. The derivation of the MM description from the QM APSLG method is rather complex and will be published elsewhere [18].

Let us consider the averages renormalizing the Hamiltonian for the R-subsystem, carrying out the summation over the spin projections. The operators of the Coulomb and the resonance interactions between the subsystems can be written as

$$V^c(q) = \sum_{\substack{pp' \in R \\ mm' \in M}} (pp' \| mm') p^+ m^+ m' p',$$

$$V^r(q) = \sum_{\substack{p \in R \\ m \in M}} v_{pm}(q)(p^+ m + m^+ p), \qquad (11)$$

where

$$(pp' \| mm') = (pp' | mm') - (pm' | mp') \qquad (12)$$

and the indices pp' and mm' refer to the one-electron states in the R- and M-subsystems, respectively. In the

latter case, the one-electron states can be taken as the HO's r_k and l_k in the M-subsystem. The averaging of the operator of Coulomb interaction between the subsystems yields:

$$\langle\langle PV^c P\rangle\rangle_M = \langle \Phi_{00}^M | PV^c P | \Phi_{00}^M \rangle$$

$$= \sum_{pp'\in R} p^+ p' \left[\sum_{mm'\in M} (pp'\|mm')\langle\langle m^+ m'\rangle\rangle_M \right]. \tag{13}$$

Since we assume that the M-subsystem is described by the wave function of the APSLG type, all the orbitals in the M-subsystem are either right (r) or left (l) orbitals of geminals. In the APSLG approximation, the averages $\langle\langle m^+ m'\rangle\rangle_M$ do not vanish only for the spin-orbitals m and m' belonging to the same geminal and can be written as

$$\langle\langle r_{k\sigma}^+ r_{k\sigma}\rangle\rangle_M = \langle 0 | g_k r_{k\sigma}^+ r_{k\sigma} g_k^+ | 0\rangle = P_k^{rr} = u_k^2 + w_k^2,$$

$$\langle\langle l_{k\sigma}^+ l_{k\sigma}\rangle\rangle_M = \langle 0 | g_k l_{k\sigma}^+ l_{k\sigma} g_k^+ | 0\rangle = P_k^{ll} = v_k^2 + w_k^2, \tag{14}$$

$$\langle\langle r_{k\sigma}^+ l_{k\sigma}\rangle\rangle_M = \langle\langle l_{k\sigma}^+ r_{k\sigma}\rangle\rangle_M = P_k^{rl} = (u_k + v_k)w_k.$$

It is also convenient to introduce the reduced Coulomb integrals

$$Y_{pp'mm'} = 2(pp'|mm') - (pm'|mp'). \tag{15}$$

Therefore, we can write the average $\langle\langle PV^c P\rangle\rangle_M$ as

$$\langle\langle PV^c P\rangle\rangle_M = \sum_{pp'\in R} \sum_\sigma p_\sigma^+ p_\sigma' \sum_{k\in M} [Y_{pp'r_k r_k} P_k^{rr}$$

$$+ Y_{pp'l_k l_k} P_k^{ll} + (Y_{pp'l_k r_k} + Y_{pp'r_k l_k})P_k^{rl}]. \tag{16}$$

The ZDO approximation assures that $p = p'$ and $m = m'$. We denote $p \in A$ and $m \in B$. In the case of $A \neq B$ we obtain the contributions of the type

$$\sum_\sigma p_\sigma^+ p_\sigma \gamma_{AB} \left[\sum_{\substack{m_k\in B \\ \tau}} \langle\langle m_{k\tau}^+ m_{k\tau}\rangle\rangle_M \right]$$

$$= 2\sum_\sigma p_\sigma^+ p_\sigma \gamma_{AB} \sum_{m_k\in B} P_k^{mm}. \tag{17}$$

The next contribution to δV^M is

$$\mathscr{V}^M = -e^2 \sum_{B'} \frac{Z_{B'}^M}{|r - R_{B'}|}$$

$$= -\sum_{pp'\in R} \sum_{B\in M} V_B^{pp'} Z_B^M \sum_\sigma p_\sigma^+ p_\sigma'. \tag{18}$$

$$V_B^{pp'} = -e^2 \int d^3 r \frac{\psi_p^*(r)\psi_{p'}(r)}{|r - R_{B'}|}$$

Taking the sum of Eqs. (17) and (18) and using the ZDO approximation, we obtain that the contribution to δV^M from the interactions of electrons belonging to different atoms equals

$$\sum_{A\in R} \sum_{p\in A\cap R} \sum_\sigma p_\sigma^+ p_\sigma \sum_{\substack{B\in M \\ B\neq A}} \gamma_{AB} Q_B^M, \tag{19}$$

where $Q_B^M = 2\sum_{m_k\in B} P_k^{mm} - Z_B^M$ is the effective charge of the atom B. The contribution from the interactions of electrons located on the orbitals belonging to different systems but centred on the same frontier atoms equals to

$$\sum_{pp'\in A} \sum_\sigma p_\sigma^+ p_\sigma' \sum_{\substack{m_k\in A \\ k\in M}} P_k^{mm} Y_{pp'mm}. \tag{20}$$

The next contribution to the effective Hamiltonian for the R-subsystem is due to the intersubsystem electron transfers

$$PV^{rr}(q, E)P = \sum_{\substack{pp'\in R \\ mm'\in M}} v_{pm}(q)v_{p'm'}(q)[(p^+ mR(E)m'^+ p')$$

$$+ (m^+ pR(E)r'^+ p')]. \tag{21}$$

The resolvent can be presented as

$$R(E) = \sum_{i\in ImQ} \frac{|i\rangle\langle i|}{E - E_i}, \tag{22}$$

where $|i\rangle$ are the states with one electron transferred from the M-subsystem to the R-subsystem and vice versa. We assume that every state $|i\rangle$ is an antisymmetrized product of ionized states $|\mu\rangle$ and $|\rho\rangle$ of the M- and R-subsystems, respectively. Moreover, we construct the states $|\mu\rangle$ by removing or adding an electron from or to the Dirac orbitals of the M-subsystem. Therefore, we can assume the energy differences in this equation to be expressed through the ionization potentials (IP) and electron affinities (EA):

$$E_i - E = \begin{cases} I_\mu - A_\rho - g_{\mu\rho} \\ I_\rho - A_\mu - g_{\rho\mu} \end{cases}. \qquad (23)$$

Now we specify the approximate form of the states $|i\rangle$ in the resolvent. First, we notice that the correlations and bonding can be accounted to the same extent as they are in the geminal Eq. (10) if one employs bonding (b) and antibonding (a) bond orbitals (BO) for the kth geminal (which are also the Dirac orbitals for this geminal):

$$\begin{cases} b_{k\sigma} = x_k l_{k\sigma} + y_k r_{k\sigma} \\ a_{k\sigma} = -y_k l_{k\sigma} + x_k r_{k\sigma} \end{cases} \qquad (x_k^2 + y_k^2 = 1). \qquad (24)$$

for constructing geminals:

$$g_k^+ = U_k b_{k\alpha}^+ b_{k\beta}^+ + V_k a_{k\alpha}^+ a_{k\beta}^+; \quad (U_k^2 + V_k^2 = 1). \qquad (25)$$

The APSLG wave function remains unchanged since the coefficient sets (U_k, V_k; x_k, y_k) and (u_k, w_k, v_k) are uniquely related:

$$\begin{cases} u_m = U_m y_m^2 + V_m x_m^2 \\ v_m = U_m x_m^2 + V_m y_m^2 \\ w_m = (U_m - V_m) x_m y_m \end{cases}. \qquad (26)$$

Using these bond orbitals, we construct the M-multiplier of the charge transfer states $|i\rangle$ in the form:

$$b_{k\sigma}^+ \prod_{l\neq k} g_l^+ |0\rangle, \quad a_{k\sigma}^+ \prod_{l\neq k} g_l^+ |0\rangle,$$

$$b_{k\sigma}^+ r_{k-\sigma}^+ l_{k-\sigma}^+ \prod_{l\neq k} g_l^+ |0\rangle, \quad a_{k\sigma}^+ r_{k-\sigma}^+ l_{k-\sigma}^+ \prod_{l\neq k} g_l^+ |0\rangle. \qquad (27)$$

The IPs and the EAs for the bond (lone pair) states within the APSLG-MINDO/3 approximation have the form:

$$I_{kb} = W_{1k}^r (y_k^2 - 2P_k^{rr}) + W_{1k}^l (x_k^2 - P_k^{ll})$$

$$+ 2W_{1k}^{rl}(x_k y_k - 2P_k^{rl}) - W_{2k}^r u_k^2$$

$$- W_{2k}^l v_k^2 - 2W_{2k}^{rl} w_k^2,$$

$$I_{ka} = W_{1k}^r (x_k^2 - 2P_k^{rr}) + W_{1k}^l (y_k^2 - P_k^{ll})$$

$$- 2W_{1k}^{rl}(x_k y_k + 2P_k^{rl}) - W_{2k}^r u_k^2 - W_{2k}^l v_k^2 - 2W_{2k}^{rl} w_k^2,$$

$$-A_{kb} = W_{1k}^r (1 + y_k^2 - 2P_k^{rr}) + W_{1k}^l (1 + x_k^2 - 2P_k^{ll})$$

$$+ 2W_{1k}^{rl}(x_k y_k - 2P_k^{rl}) + W_{2k}^r (y_k^2 - u_k^2)$$

$$+ W_{2k}^l (x_k^2 - v_k^2) + 2W_{2k}^{rl}(1 - w_k^2),$$

$$-A_{ka} = W_{1k}^r (1 + x_k^2 - 2P_k^{rr}) + W_{1k}^l (1 + y_k^2 - 2P_k^{ll})$$

$$- 2W_{1k}^{rl}(x_k y_k + 2P_k^{rl}) + W_{2k}^r (x_k^2 - u_k^2)$$

$$+ W_{2k}^l (y_k^2 - v_k^2) + 2W_{2k}^{rl}(1 - w_k^2). \qquad (28)$$

where these quantities are expressed through the parameters of the effective Hamiltonian for the kth bond in the APSLG-MINDO/3 approximation, which can be written as

$$H_k^{\text{eff}} = W_{1k}^r \sum_\sigma r_{k\sigma}^+ r_{k\sigma} + W_{1k}^l \sum_\sigma l_{k\sigma}^+ l_{k\sigma}$$

$$+ W_{1k}^{rl} \sum_\sigma (r_{k\sigma}^+ l_{k\sigma} + l_{k\sigma}^+ r_{k\sigma}) + W_{2k}^r r_{k\alpha}^+ r_{k\beta}^+ r_{k\beta} r_{k\alpha}$$

$$+ W_{2k}^l l_{k\alpha}^+ l_{k\beta}^+ l_{k\beta} l_{k\alpha} + W_{2k}^{rl} \sum_\sigma r_{k\alpha}^+ l_{k-\sigma}^+ l_{k-\sigma} r_{k\sigma}, \qquad (29)$$

with

$$W_{1k}^r = \left(U_k^{A_k} - \sum_{B' \neq A_k} \gamma_{A_k B'} Z_{B'} \right) + \sum_{t_n \in A_k, n \neq k} Y_{r_k r_k t_n t_n}^{A_k} P_n^{tt}$$

$$+ 2 \sum_{B' \neq A_k} \gamma_{A_k B'} \sum_{t_n \in B', n \neq k} P_n^{tt},$$

$$W_{1k}^l = \left(U_k^{B_k} - \sum_{B' \neq B_k} \gamma_{B_k B'} Z_{B'} \right) + \sum_{t_n \in A_k, n \neq k} Y_{l_k l_k t_n t_n}^{B_k} P_n^{tt}$$

$$+ 2 \sum_{B' \neq B_k} \gamma_{B_k B'} \sum_{t_n \in B', n \neq k} P_n^{tt},$$

$$W_{1k}^{rl} = -\beta_k, \qquad W_{2k}^r = (r_k r_k | r_k r_k)^{A_k},$$

$$W_{2k}^l = (l_k l_k | l_k l_k)^{B_k}, \qquad W_{2k}^{rl} = \gamma_{A_k B_k}. \qquad (30)$$

The resolvent contribution from the first projection to the effective Hamiltonian of the R-subsystem can be written in the form including the ionized states of the R-subsystem:

$$\langle\langle P V^{rr}(q, E) P \rangle\rangle_M$$

$$= - \sum_{pp' \in R} \sum_{\sigma} \sum_{k \in M} \sum_{ij \in \{r, l\}} \sum_{f \in \{a, b\}} v_{pi_k} v_{p' j_k}$$

$$\times \left(\sum_{\rho \in Im O_R(N_R - 1)} p_\sigma^+ |\rho\rangle\langle\rho| p'_\sigma \frac{\theta_{if}^k \theta_{jf}^k}{I_\rho - A_{kf} - g_{\rho f_k}} \right.$$

$$\left. + \sum_{\rho \in Im O_R(N_R + 1)} p_\sigma |\rho\rangle\langle\rho| p'^+_\sigma \frac{\eta_{if}^k \eta_{jf}^k}{I_{kf} - A_\rho - g_{f_k \rho}} \right), \qquad (31)$$

where we use the vacuum averages

$$\theta_{if}^k = \langle 0 | g_k i_{k\alpha} f_{k\beta}^+ r_{k\alpha}^+ l_{k\alpha}^+ | 0 \rangle,$$

$$\eta_{if}^k = \langle 0 | g_k i_{k\alpha}^+ f_{k\beta}^+ | 0 \rangle \qquad (32)$$

which can be easily expressed in terms of the parameters of the APSLG wave function in the

representations Eqs. (10), (25) and (26):

$$\theta_{rb}^k = y_k w_k + x_k v_k, \quad \theta_{ra}^k = x_k w_k - y_k v_k,$$

$$\theta_{lb}^k = -x_k w_k - y_k u_k, \quad \theta_{la}^k = y_k w_k - x_k u_k;$$

$$\eta_{rb}^k = y_k u_k + x_k w_k, \quad \eta_{ra}^k = x_k u_k - y_k w_k,$$

$$\eta_{lb}^k = y_k w_k + x_k v_k, \quad \eta_{la}^k = x_k w_k - y_k v_k. \qquad (33)$$

Now we consider rather cumbersome contribution that arise during the second projection:

$$\langle \Phi_{00}^M | P \mathcal{W}(q, E) P \mathcal{Q} \mathcal{R}(\omega) \mathcal{Q} P \mathcal{W}(q, E) P | \Phi_{00}^M \rangle. \qquad (34)$$

In order to do that we reconsider the substance of the notion of the quantum character of the R-subsystem and of the classical one of the M-subsystem. As it is mentioned in Ref. [19], the quantum character of a part of a molecular system manifests itself in its spectrum which possesses excited states in a narrow energy range close to its ground state. It makes it possible to observe several quantum states in experiment at least in principle. By contrast, the characteristic of a classical part of molecular system is that its properties are determined by its ground state only so that the energies of its excited states are very high as compared to the energy range probed experimentally. In the present derivation, we are interested in obtaining the effective Hamiltonian for the states of the R-(quantum) subsystem close to its ground state. We assume that the dependence of the resolvent on ω is weak and the ω values of interest are much smaller than the resolvent poles which are all higher than the first excitation energy in the M- (classical) subsystem which in its turn is higher than the excitation energies of interest in the R-subsystem. Therefore, we can turn to the limit $\omega \to 0$ in the expression (34). The resolvent can be represented as

$$\mathcal{R}(0) = \lim_{\omega \to 0} \mathcal{R}(\omega) = \lim_{\omega \to 0} \sum_{\substack{\rho \\ \mu \neq 0}} \frac{|\rho, \mu\rangle\langle\rho, \mu|}{\omega - \omega_{\rho\mu}}$$

$$= - \sum_{\substack{\rho \\ \mu \neq 0}} \frac{|\rho, \mu\rangle\langle\rho, \mu|}{\epsilon_\rho + \epsilon_\mu}, \qquad (35)$$

where the sum excludes the states having the ground state of the M-subsystem as the multiplier and ϵ_ρ and ϵ_μ are the energies of the excitations in the R- and

M-subsystems, respectively. The contribution Eq. (34) can be expressed as:

$$\langle \Phi_{00}^M | P\mathscr{W}(q,E)P\mathscr{2R}(0)\mathscr{2}P\mathscr{W}(q,E)P | \Phi_{00}^M \rangle$$

$$= \langle \Phi_{00}^M | PV^c P\mathscr{2R}(0)\mathscr{2}PV^c P | \Phi_{00}^M \rangle$$

$$+ \langle \Phi_{00}^M | PV^{rr} P\mathscr{2R}(0)\mathscr{2}PV^{rr} P | \Phi_{00}^M \rangle$$

$$+ \langle \Phi_{00}^M | P\mathscr{V}^R P\mathscr{2R}(0)\mathscr{2}P\mathscr{V}^R P | \Phi_{00}^M \rangle$$

$$+ 2\langle \Phi_{00}^M | PV^c P\mathscr{2R}(0)\mathscr{2}PV^{rr} P | \Phi_{00}^M \rangle$$

$$+ 2\langle \Phi_{00}^M | PV^c P\mathscr{2R}(0)\mathscr{2}P\mathscr{V}^R P | \Phi_{00}^M \rangle$$

$$+ 2\langle \Phi_{00}^M | PV^{rr} P\mathscr{2R}(0)\mathscr{2}P\mathscr{V}^R P | \Phi_{00}^M \rangle. \tag{36}$$

We will write these averages explicitly. Since the R-subsystem is quantum and thus has low-lying excited states but the M-subsystem is classical and its excitation energies are high and thus $\epsilon_\rho \ll \epsilon_\mu$ and ϵ_ρ can be neglected in Eq. (35) as compared to ϵ_μ. Using the symmetry with respect to the spin indices, we obtain:

$$\langle \Phi_{00}^M | PV^c P\mathscr{2R}(0)\mathscr{2}PV^c P | \Phi_{00}^M \rangle$$

$$= \sum_{pp'qq' \in R} \sum_{kn \in M} \sum_{ii'jj' \in \{r,l\}}$$

$$\times \Bigg[\sum_{\substack{\sigma\tau \\ \sigma'\tau'}} p_\sigma^+ p'_\sigma (1 - |0_R\rangle\langle 0_R|) q_\tau^+ q'_\tau$$

$$\times \prod_{i_{k\sigma'} i'_{n\sigma'} j_{nr'} j'_{kr'}}^{M} ((pp'|i_k i'_n) - \delta_{\sigma\sigma'}(pi'_n|i_k p'))((qq'|j_n j'_k)$$

$$- \delta_{\tau\tau'}(qj'_k|j_n q')) + \sum_\sigma p_\sigma^+ p'_{-\sigma} (1 - |0_R\rangle\langle 0_R|)$$

$$\times q_{-\sigma}^+ q'_\sigma (pi'_n|i_k p')(qj'_k|j_n q') \prod_{i_{k-\sigma'} i'_{n\sigma} j_{n\sigma} j'_{k-\sigma}}^{M} \Bigg], \tag{37}$$

where the state $|0_R\rangle$ is the ground state of the free R-subsystem. In this expression, we use the zero-frequency polarization propagators of the M-subsystem [14], which are defined by the expression

$$\prod_{mm'nn'}^{M} = - \sum_{\mu \neq 0} \frac{\langle \Phi_{00}^M | m^+ m' | \mu \rangle \langle \mu | n^+ n' | \Phi_{00}^M \rangle}{\epsilon_\mu}. \tag{38}$$

to which the excitations in the M-subsystem contribute. The APSLG form of the ground-state wave function implies specific classification for these excitations: they are either intrabond singlet–singlet or singlet–triplet excitations or the inter-bond one- and two-electron transfers. We present the explicit expressions for the contributions to the polarization propagator from the excitations of different types.

1. $\prod_{i_{k\sigma} i'_{k\sigma} j_{k\tau} j'_{k\tau}}^{M}$. The excited state $|\mu\rangle$ is one of the states $|\mu_{1,2}\rangle = g_k^{(1,2)+} \prod_{k' \neq k} g_{k'}^+ |0\rangle$ (these are excited singlet configurations of the kth geminal with others unchanged) and

$$|\mu_3\rangle = \frac{1}{\sqrt{2}}(r_{k\alpha}^+ l_{k\beta}^+ - l_{k\alpha}^+ r_{k\beta}^+) \prod_{k' \neq k} g_{k'}^+ |0\rangle$$

(the triplet configuration with $s_z = 0$ of the kth geminal with others unchanged). Therefore,

$$\prod_{i_{k\sigma} i'_{k\sigma} j_{k\tau} j'_{k\tau}}^{M} = - \sum_{s \in \{1-3\}} \frac{\langle \Phi_{00}^M | i_{k\sigma}^+ i'_{k\sigma} | \mu_s \rangle \langle \mu_s | j_{k\tau}^+ j'_{k\tau} | \Phi_{00}^M \rangle}{\epsilon_{\mu_s}}. \tag{39}$$

The energies of excitations ϵ_{μ_s} in the APSLG-MINDO/3 approximation Refs. [15,16] are:

$$\epsilon_{\mu_{s=1,2}} = 2W_{1k}^r(u_k^{(s)2} + w_k^{(s)2} - P_k^{rr})$$

$$+ 2W_{1k}^l(v_k^{(s)2} + w_k^{(s)2} - P_k^{ll}) + W_{2k}^r(u_k^{(s)2} - u_k^2)$$

$$+ W_{2k}^l(v_k^{(s)2} - v_k^2) + 4W_{1k}^{rl}[(u_k^{(s)} + v_k^{(s)})w_k^{(s)} - P_k^{rl}]$$

$$+ 2W_{2k}^{rl}(w_k^{(s)2} - w_k^2), \tag{40}$$

$$\epsilon_{\mu_3} = (W_{1k}^r - W_{1k}^l)(v_k^2 - u_k^2) - W_{2k}^r u_k^2 - W_{2k}^l v_k^2$$

$$- 4W_{1k}^{rl}P_k^{rl} + W_{2k}^{rl}(u_k^2 + v_k^2). \tag{41}$$

The matrix elements entering the expression for the polarization propagator are

$$\langle \Phi_{00}^M | r_{k\sigma}^+ r_{k\sigma} | \mu_{s=1,2} \rangle = u_k u_k^{(s)} + w_k w_k^{(s)},$$

$$\langle \Phi_{00}^M | l_{k\sigma}^+ l_{k\sigma} | \mu_{s=1,2} \rangle = v_k v_k^{(s)} + w_k w_k^{(s)},$$

$$\langle \Phi_{00}^M | r_{k\sigma}^+ l_{k\sigma} | \mu_{s=1,2} \rangle = u_k w_k^{(s)} + w_k v_k^{(s)},$$

$$\langle \Phi_{00}^M | l_{k\sigma}^+ r_{k\sigma} | \mu_{s=1,2} \rangle = w_k u_k^{(s)} + v_k w_k^{(s)};$$

$$\tag{42}$$

$$\langle \Phi_{00}^M | r_{k\alpha}^+ r_{k\alpha} | \mu_3 \rangle = \frac{w_k}{\sqrt{2}}, \quad \langle \Phi_{00}^M | l_{k\alpha}^+ l_{k\alpha} | \mu_3 \rangle = -\frac{w_k}{\sqrt{2}},$$

$$\langle \Phi_{00}^M | r_{k\alpha}^+ l_{k\alpha} | \mu_3 \rangle = \frac{-u_k}{\sqrt{2}}, \quad \langle \Phi_{00}^M | l_{k\alpha}^+ r_{k\alpha} | \mu_3 \rangle = \frac{v_k}{\sqrt{2}}$$

$$\langle \Phi_{00}^M | i_{k\beta}^+ j_{k\beta} | \mu_3 \rangle = -\langle \Phi_{00}^M | i_{k\alpha}^+ j_{k\alpha} | \mu_3 \rangle. \tag{43}$$

For real orbitals the following $\langle \mu_s | i^+ j | \Phi_{00}^M \rangle = \langle \Phi_{00}^M | j^+ i | \mu_s \rangle$ holds.

2. $\prod_{i_{k-\sigma} i'_{k\sigma} j_{k\sigma} j'_{k-\sigma}}^M$. The excited state

$$|\mu_4 \rangle = r_{k\sigma}^+ l_{k\sigma}^+ \prod_{k' \neq k} g_{k'}^+ |0\rangle$$

(the triplet configuration with $s_z = 1$ for $\sigma = \alpha$ and $s_z = -1$ for $\sigma = \beta$ in the kth geminal with others unchanged).

$$\langle \Phi_{00}^M | i_{k-\sigma}^+ i'_{k\sigma} | \mu_4 \rangle = \langle 0 | g_k i_{k-\sigma}^+ i'_{k\sigma} r_{k\sigma}^+ l_{k\sigma}^+ | 0 \rangle. \tag{44}$$

The energies of such excitations obviously equal to respective energies of excitations to the triplet states with $s_z = 0$, i.e. $\epsilon_{\mu_4} = \epsilon_{\mu_3}$. The matrix elements equal to

$$\langle \Phi_{00}^M | r_{k\alpha}^+ r_{k\beta} | \mu_4 \rangle = w_k, \quad \langle \Phi_{00}^M | l_{k\alpha}^+ l_{k\beta} | \mu_4 \rangle = -w_k,$$

$$\langle \Phi_{00}^M | l_{k\alpha}^+ r_{k\beta} | \mu_4 \rangle = v_k, \quad \langle \Phi_{00}^M | r_{k\alpha}^+ l_{k\beta} | \mu_4 \rangle = -u_k \tag{45}$$

$$\langle \Phi_{00}^M | i_{k\beta}^+ j_{k\alpha} | \mu_4 \rangle = -\langle \Phi_{00}^M | i_{k\alpha}^+ j_{k\beta} | \mu_4 \rangle.$$

3. $\prod_{i_{k\sigma} i'_{n\sigma} j_{n\tau} j'_{k\tau}}^M$ ($n \neq k$). This polarization propagator differs from zero, only for $\sigma = \tau$. The excited state involved is

$$|\mu_5 \rangle = h_{n-\sigma}^+ r_{n\sigma}^+ l_{n\sigma}^+ f_{k-\sigma}^+ \prod_{k' \neq k,n} g_{k'}^+ |0\rangle,$$

where f and h are either b or a BOs. The energy of the excitation is estimated as

$$\epsilon_5 = I_{kf} - A_{nh} - g_{f_k h_n}. \tag{46}$$

The IPs and the EAs (I_{kf}, A_{nh}) are given above. Therefore, we specify here only $g_{f_k h_n}$. It is convenient to introduce new quantities c_{fi}, which are amplitudes of the ith

HO (r or l) in the BO f (a or b) given by Eq. (24). Then

$$g_{f_k h_n} = \sum_{ij \in \{r,l\}} [Y_{i_k i_k j_n j_n} (2P_k^{ii}(1 + c_{f_k i_k}^2) + 2P_n^{jj} c_{h_n j_n}^2)$$

$$- (i_k i_k | j_n j_n)(1 + c_{f_k i_k}^2) c_{h_n j_n}^2 + (i_k j_n | i_k j_n) c_{f_k i_k}^2 c_{h_n j_n}^2]. \tag{47}$$

The required matrix elements are

$$\langle \Phi_{00}^M | i_{k\sigma}^+ i'_{n\sigma} | \mu_5 \rangle = \eta_{if}^k \theta_{i'h}^n. \tag{48}$$

4. $\prod_{i_{k-\sigma} i'_{n\sigma} j_{n\sigma} j'_{k-\sigma}}^M$ ($n \neq k$). The excited state is

$$|\mu_6 \rangle = h_{n-\sigma}^+ r_{n\sigma}^+ l_{n\sigma}^+ f_{k\sigma}^+ \prod_{k' \neq k,n} g_{k'}^+ |0\rangle,$$

where f and h are either b or a. The energy of the excitation is estimated as

$$\epsilon_6 = I_{kf} - A_{nh} - g'_{f_k h_n}, \tag{49}$$

where

$$g'_{f_k h_n} = \sum_{ij \in \{r,l\}} [Y_{i_k i_k j_n j_n} (2P_k^{ii}(1 + c_{f_k i_k}^2) + 2P_n^{jj} c_{h_n j_n}^2)$$

$$- (i_k i_k | j_n j_n)(1 + c_{f_k i_k}^2) c_{h_n j_n}^2 + (i_k j_n | i_k j_n) c_{h_n j_n}^2]. \tag{50}$$

The required matrix elements are

$$\langle \Phi_{00}^M | i_{k-\sigma}^+ i'_{n\sigma} | \mu_6 \rangle = -\eta_{if}^k \theta_{i'h}^n. \tag{51}$$

If the ZDO approximation is used for the two-center Coulomb interaction parameters, the contribution Eq. (34) into the effective Hamiltonian for the R-subsystem simplifies significantly:

$$\langle \Phi_{00}^M | PV^c P \mathcal{2R}(0) \mathcal{2} V^c P | \Phi_{00}^M \rangle = \sum_{pq \in R} \sum_{k \in M} \sum_{ij \in \{r,l\}}$$

$$\times \Bigg[\sum_{\substack{\sigma\tau \\ \sigma'\tau'}} p_\sigma^+ p_\sigma (1 - |0_R\rangle\langle 0_R|) q_\tau^+ q_\tau$$

$$\times \prod_{i_{k\sigma'} i'_{k\sigma'} j_{k\tau'} j'_{k\tau'}}^M ((pp|i_k i_k) - \delta_{\sigma\sigma'}(pi_k|i_k p))((qq|j_k j_k)$$

$$- \delta_{\tau\tau'}(qj_k|j_k q)) + \sum_\sigma p_\sigma^+ p_{-\sigma}(1 - |0_R\rangle\langle 0_R|) q_{-\sigma}^+ q_\sigma$$

$$\times (pi_k|i_k p)(qj_k|j_k q) \prod_{i_{k-\sigma} i_{k\sigma} j_{k\sigma} j_{k-\sigma}}^M \Bigg]. \tag{52}$$

The next contribution to the effective Hamiltonian can be presented as a sum of one-geminal and two-geminal contributions:

$$\langle \Phi_{00}^M | PV^{rr} P \mathscr{Q} \mathscr{R}(0) \mathscr{Q} PV^{rr} P | \Phi_{00}^M \rangle$$

$$= \sum_k \langle \Phi_{00}^M | PV^{rr} P \mathscr{Q} \mathscr{R}(0) \mathscr{Q} PV^{rr} P | \Phi_{00}^M \rangle_k$$

$$+ \sum_{k \neq n} \langle \Phi_{00}^M | PV^{rr} P \mathscr{Q} \mathscr{R}(0) \mathscr{Q} PV^{rr} P | \Phi_{00}^M \rangle_{kn}. \quad (53)$$

The one-geminal contribution has the form

$$\langle \Phi_{00}^M | PV^{rr} P \mathscr{Q} \mathscr{R}(0) \mathscr{Q} PV^{rr} P | \Phi_{00}^M \rangle_k$$

$$= \sum_{\substack{pp' \in R \\ qq' \in R}} \sum_{\substack{ii' jj' \in \{r,l\} \\ fh \in \{a,b\}}} \sum_{\substack{\sigma\tau \\ ss'}} v_{pi_k} v_{p'i'_k} v_{qj_k} v_{q'j'_k}$$

$$\times \Bigg[\sum_{\rho_1,\rho_2 \in ImO_R(N_R+1)} \frac{A_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) \Xi_{i_{k\sigma} i'_{ks} j_{ks'} j'_{k\tau}}^{f_{k-\sigma} h_{k-\tau}}}{(I_{kf} - A_{\rho_1} - g_{f_k\rho_1})(I_{kh} - A_{\rho_2} - g_{h_k\rho_2})}$$

$$- \sum_{\substack{\rho_1 \in ImO_R(N_R+1) \\ \rho_2 \in ImO_R(N_R-1)}} (-1)^{\delta_{jj'}} \frac{B_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) \Xi_{i_{k\sigma} i'_{ks} \tilde{j}_{ks'} \tilde{j}'_{k\tau}}^{f_{k-\sigma} h_{k-\tau}}}{(I_{kf} - A_{\rho_1} - g_{f_k\rho_1})(I_{\rho_2} - A_{kh} - g_{\rho_2 h_k})}$$

$$- \sum_{\substack{\rho_1 \in ImO_R(N_R-1) \\ \rho_2 \in ImO_R(N_R+1)}} (-1)^{\delta_{ii'}} \frac{C_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) \Xi_{\tilde{i}_{k\sigma} \tilde{i}'_{ks} j_{ks'} j'_{k\tau}}^{f_{k-\sigma} h_{k-\tau}}}{(I_{\rho_1} - A_{kf} - g_{\rho_1 f_k})(I_{kh} - A_{\rho_2} - g_{h_k\rho_2})}$$

$$+ \sum_{\rho_1,\rho_2 \in ImO_R(N_R-1)} (-1)^{\delta_{ii'} + \delta_{jj'}}$$

$$\times \frac{D_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) \Xi_{\tilde{i}_{k\sigma} \tilde{i}'_{ks} \tilde{j}_{ks'} \tilde{j}'_{k\tau}}^{f_{k-\sigma} h_{k-\tau}}}{(I_{\rho_1} - A_{kf} - g_{\rho_1 f_k})(I_{\rho_2} - A_{kh} - g_{\rho_2 h_k})} \Bigg], \quad (54)$$

while the two-geminal contributions have the form

$$\langle \Phi_{00}^M | PV^{rr} P \mathscr{Q} \mathscr{R}(0) \mathscr{Q} PV^{rr} P | \Phi_{00}^M \rangle_{kn}$$

$$= \sum_{\substack{pp' \in R \\ qq' \in R}} \sum_{\substack{ii' jj' \in \{r,l\} \\ f \in \{a,b\}}} \sum_{\sigma\varsigma} v_{pi_k} v_{p'i'_n} v_{qj_n} v_{q'j'_k}$$

$$\times \Bigg[\sum_{\rho_1,\rho_2 \in ImO_R(N_R+1)} \frac{A_{pp'qq'}^{\sigma\sigma\varsigma\varsigma}(\rho_1\rho_2) \Xi_{i_{k\sigma} i'_{n\varsigma} j_{n\varsigma} j'_{k\sigma}}^{f_{k-\sigma} f_{k-\sigma}}}{(I_{kf} - A_{\rho_1} - g_{f_k\rho_1})(I_{kf} - A_{\rho_2} - g_{f_k\rho_2})}$$

$$+ \sum_{\rho_1,\rho_2 \in ImO_R(N_R-1)} \frac{D_{pp'qq'}^{\sigma\sigma\varsigma\varsigma}(\rho_1\rho_2) \Xi_{i'_{n\varsigma} i_{k\sigma} j'_{k\sigma} j_{n\varsigma}}^{f_{k-\sigma} f_{k-\sigma}}}{(I_{\rho_1} - A_{kf} - g_{\rho_1 f_k})(I_{\rho_2} - A_{kf} - g_{\rho_2 f_k})} \Bigg]$$

$$- \sum_{\substack{pp' \in R \\ qq' \in R}} \sum_{\substack{ii' jj' \in \{r,l\} \\ fh \in \{a,b\}}} \sum_{\sigma\varsigma} v_{pi_k} v_{p'i'_n} v_{qj_k} v_{q'j'_n}(-1)^{\delta_{\sigma\varsigma}}$$

$$\times \Bigg[\sum_{\substack{\rho_1 \in ImO_R(N_R+1) \\ \rho_2 \in ImO_R(N_R-1)}} \frac{B_{pp'qq'}^{\sigma\sigma\varsigma\varsigma}(\rho_1\rho_2) \Xi_{i_{k\sigma} i'_{n\varsigma} j'_{n\varsigma} j_{k\sigma}}^{f_{k-\sigma} h_{n-\varsigma}}}{(I_{kf} - A_{\rho_1} - g_{f_k\rho_1})(I_{\rho_2} - A_{nh} - g_{\rho_2 h_n})}$$

$$+ \sum_{\substack{\rho_1 \in ImO_R(N_R-1) \\ \rho_2 \in ImO_R(N_R+1)}} \frac{C_{pp'qq'}^{\sigma\sigma\varsigma\varsigma}(\rho_1\rho_2) \Xi_{i'_{n\varsigma} i_{k\sigma} j_{k\sigma} j'_{n\varsigma}}^{f_{k-\sigma} h_{n-\varsigma}}}{(I_{\rho_1} - A_{kf} - g_{\rho_1 f_k})(I_{nh} - A_{\rho_2} - g_{h_n\rho_2})} \Bigg], \quad (55)$$

where $\tilde{\iota} = r$ for $i = l$ and $\tilde{\iota} = l$ for $i = r$. Operators can be represented as

$$A_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) = \delta_{s\sigma} \delta_{s'\tau} p_\sigma |\rho_1\rangle\langle\rho_1| p'^+_\sigma$$

$$\times (1 - |0_R\rangle\langle 0_R|) q_\tau |\rho_2\rangle\langle\rho_2| q'^+_\tau$$

$$+ \delta_{ss'} \delta_{\sigma\tau} \delta_{s-\sigma} p_\sigma |\rho_1\rangle\langle\rho_1| p'^+_{-\sigma}$$

$$\times (1 - |0_R\rangle\langle 0_R|) q_{-\sigma} |\rho_2\rangle\langle\rho_2| q'^+_\sigma,$$

$$B_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) = \delta_{s\sigma} \delta_{s'\tau} p_\sigma |\rho_1\rangle\langle\rho_1| p'^+_\sigma$$

$$\times (1 - |0_R\rangle\langle 0_R|) q^+_\tau |\rho_2\rangle\langle\rho_2| q'_\tau$$

$$- \delta_{ss'} \delta_{\sigma\tau} \delta_{s-\sigma} p_\sigma |\rho_1\rangle\langle\rho_1| p'^+_{-\sigma}$$

$$\times (1 - |0_R\rangle\langle 0_R|) q^+_{-\sigma} |\rho_2\rangle\langle\rho_2| q'_\sigma,$$

$$C^{\sigma\tau ss'}_{pp'qq'}(\rho_1\rho_2) = \delta_{\varsigma\sigma}\delta_{s'\tau}p^+_\sigma|\rho_1\rangle\langle\rho_1|p'_\sigma$$

$$\times(1 - |0_R\rangle\langle 0_R|)q_\tau|\rho_2\rangle\langle\rho_2|q'^+_\tau$$

$$-\delta_{ss'}\delta_{\sigma\tau}\delta_{s-\sigma}p^+_\sigma|\rho_1\rangle\langle\rho_1|p'_{-\sigma}$$

$$\times(1 - |0_R\rangle\langle 0_R|)q_{-\sigma}|\rho_2\rangle\langle\rho_2|q'^+_\sigma,$$

$$D^{\sigma\tau ss'}_{pp'qq'}(\rho_1\rho_2) = \delta_{\varsigma\sigma}\delta_{s'\tau}p^+_\sigma|\rho_1\rangle\langle\rho_1|p'_\sigma$$

$$\times(1 - |0_R\rangle\langle 0_R|)q^+_\tau|\rho_2\rangle\langle\rho_2|q'_\tau$$

$$+\delta_{ss'}\delta_{\sigma\tau}\delta_{s-\sigma}p^+_\sigma|\rho_1\rangle\langle\rho_1|p'_{-\sigma}$$

$$\times(1 - |0_R\rangle\langle 0_R|)q^+_{-\sigma}|\rho_2\rangle\langle\rho_2|q'_\sigma. \quad (56)$$

Also we introduce the quantities

$$\Xi^{fh}_{ii'jj'} = -\sum_{\mu\neq 0}\frac{\langle\Phi^M_{00}|i^+f^+fi'|\mu\rangle\langle\mu|j^+h^+hj'|\Phi^M_{00}\rangle}{\epsilon_\mu}, \quad (57)$$

which in general case cannot be reduced to the polarization propagators. Now we consider different cases (the energies of excitations were determined above).

1. $\Xi^{f_{k-\sigma}h_{k-\sigma}}_{i_{k\sigma}i'_{k\sigma}j_{k\sigma}j'_{k\sigma}}$. The excited state $|\mu\rangle$ is one of $|\mu_{1,2,3}\rangle$, defined above. We have to determine only matrix elements.

$$\langle\Phi^M_{00}|i^+_{k\sigma}f^+_{k-\sigma}f_{k-\sigma}i'_{k\sigma}|\mu_{s=1,2}\rangle = \theta^k_{if}\theta^k_{i'f}(s), \quad (58)$$

where $\theta^k_{if}(s)$ coincides with θ^k_{if} defined above (see Eq. (32)), but with u_k, v_k, and w_k changed to $u^{(s)}_k$, $v^{(s)}_k$, and $w^{(s)}_k$.

$$\langle\Phi^M_{00}|i^+_{k\sigma}f^+_{k-\sigma}f_{k-\sigma}i'_{k\sigma}|\mu_3\rangle = \frac{1}{\sqrt{2}}\theta^k_{if}(\delta_{i'r}c_{f_kl_k} - \delta_{i'l}c_{f_kr_k}). \quad (59)$$

2. $\Xi^{f_{k\sigma}h_{k\sigma}}_{i_{k-\sigma}i'_{k\sigma}j_{k\sigma}j'_{k-\sigma}}$. The excited state is $|\mu_4\rangle$. The matrix elements are

$$\langle\Phi^M_{00}|i^+_{k-\sigma}f^+_{k\sigma}f_{k\sigma}i'_{k\sigma}|\mu_4\rangle = (-1)^{\delta_{\sigma\alpha}}\theta^k_{if}(\delta_{i'r}c_{f_kl_k} - \delta_{i'l}c_{f_kr_k}). \quad (60)$$

3. $\Xi^{f_{k-\sigma}f_{k-\sigma}}_{i_{k\sigma}i'_{n\sigma}j_{n\sigma}j'_{k\sigma}}$. The excited state is of $|\mu_5\rangle$ type. The required matrix elements are

$$\langle\Phi^M_{00}|i^+_{k\sigma}f^+_{k-\sigma}f_{k-\sigma}i'_{n\sigma}|\mu_5\rangle = \eta^k_{if}\theta^n_{i'h}. \quad (61)$$

4. $\Xi^{f_{k-\sigma}f_{k-\sigma}}_{i'_{n\sigma}i_{k\sigma}j'_{k\sigma}j_{n\sigma}}$. The excited state is of $|\mu_5\rangle$ type:

$$f^+_{k-\sigma}r^+_{k\sigma}l^+_{k\sigma}h^+_{n-\sigma}\prod_{k'\neq k,n}g^+_{k'}|0\rangle.$$

The required matrix elements are

$$\langle\Phi^M_{00}|i'^+_{n\sigma}f^+_{k-\sigma}f_{k-\sigma}i_{k\sigma}|\mu_5\rangle = \theta^k_{if}\eta^n_{i'f}. \quad (62)$$

5. $\Xi^{f_{k\sigma}f_{k\sigma}}_{i_{k-\sigma}i'_{n\sigma}j_{n\sigma}j'_{k-\sigma}}$. The excited state is of $|\mu_6\rangle$ type. The required matrix elements are

$$\langle\Phi^M_{00}|i^+_{k-\sigma}f^+_{k\sigma}f_{k\sigma}i'_{n\sigma}|\mu_6\rangle = -\eta^k_{if}\theta^n_{i'h}. \quad (63)$$

6. $\Xi^{f_{k\sigma}f_{k\sigma}}_{i'_{n\sigma}i_{k-\sigma}j'_{k-\sigma}j_{n\sigma}}$. The excited state is of $|\mu_6\rangle$ type:

$$f^+_{k\sigma}r^+_{k-\sigma}l^+_{k-\sigma}h^+_{n-\sigma}\prod_{k'\neq k,n}g^+_{k'}|0\rangle.$$

The required matrix elements are

$$\langle\Phi^M_{00}|i'^+_{n\sigma}f^+_{k\sigma}f_{k\sigma}i_{k-\sigma}|\mu_6\rangle = -\theta^k_{if}\eta^n_{i'h}. \quad (64)$$

Other quantities Ξ do not contain new averages and can be obtained using expressions written above.

Also we can note that

$$\prod\nolimits^M_{i_{k\sigma}i'_{k\sigma}j_{k\sigma}j'_{k\sigma}} = \sum_{fh\in\{r,l\}}\Xi^{f_{k-\sigma}h_{k-\sigma}}_{i_{k\sigma}i'_{k\sigma}j_{k\sigma}j'_{k\sigma}} \quad (65)$$

and analogous expressions can be obtained for other types of Ξ, i.e. the summation over upper indices of Ξs gives the polarization propagator with respective lower indices. Therefore, if we use the approximation that the energies of electron transfer from (or to) the kth bond of the M-subsystem to (or from) R-subsystem do not depend on the type of the resultant state of the bond (or equivalently consider only one excited state of each type for every geminal) we obtain this contribution to the effective Hamiltonian for the R-subsystem to be

expressed in terms of the polarization propagators:

$$\langle \Phi_{00}^M | PV^{rr} P \mathcal{Q} \mathcal{R}(0) \mathcal{Q} PV^{rr} P | \Phi_{00}^M \rangle_k$$

$$
= \sum_{\substack{pp' \in R \\ qq' \in R}} \sum_{ii'jj' \in \{r,l\}} \sum_{\substack{\sigma\tau \\ ss'}} v_{pi_k} v_{p'i'_k} v_{qj_k} v_{q'j'_k} \left[\sum_{\rho_1,\rho_2 \in ImO_R(N_R+1)} \frac{A_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) \prod_{i_{k\sigma}i'_{ks}j_{ks'}j'_{k\tau}}^M}{(I_k - A_{\rho_1} - g_{k\rho_1})(I_k - A_{\rho_2} - g_{k\rho_2})} \right.
$$

$$
- \sum_{\substack{\rho_1 \in ImO_R(N_R+1) \\ \rho_2 \in ImO_R(N_R-1)}} (-1)^{\delta_{jj'}} \frac{B_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) \prod_{i_{k\sigma}i'_{ks}\tilde{j}_{ks'}\tilde{j}'_{k\tau}}^M}{(I_k - A_{\rho_1} - g_{k\rho_1})(I_{\rho_2} - A_k - g_{\rho_2 k})}
$$

$$
- \sum_{\substack{\rho_1 \in ImO_R(N_R-1) \\ \rho_2 \in ImO_R(N_R+1)}} (-1)^{\delta_{ii'}} \frac{C_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) \prod_{\tilde{i}_{k\sigma}\tilde{i}'_{ks}j_{ks'}j'_{k\tau}}^M}{(I_{\rho_1} - A_k - g_{\rho_1 k})(I_k - A_{\rho_2} - g_{k\rho_2})}
$$

$$
\left. + \sum_{\rho_1,\rho_2 \in ImO_R(N_R-1)} (-1)^{\delta_{ii'}+\delta_{jj'}} \frac{D_{pp'qq'}^{\sigma\tau ss'}(\rho_1\rho_2) \prod_{\tilde{i}_{k\sigma}\tilde{i}'_{ks}\tilde{j}_{ks'}\tilde{j}'_{k\tau}}^M}{(I_{\rho_1} - A_k - g_{\rho_1 k})(I_{\rho_2} - A_k - g_{\rho_2 k})} \right], \tag{66}
$$

and

$$\langle \Phi_{00}^M | PV^{rr} P \mathcal{Q} \mathcal{R}(0) \mathcal{Q} PV^{rr} P | \Phi_{00}^M \rangle_{kn}$$

$$
= \sum_{\substack{pp' \in R \\ qq' \in R}} \sum_{ii'jj' \in \{r,l\}} \sum_{\sigma s} v_{pi_k} v_{p'i'_n} v_{qj_n} v_{q'j'_k} \left[\sum_{\rho_1,\rho_2 \in ImO_R(N_R+1)} \frac{A_{pp'qq'}^{\sigma\sigma ss}(\rho_1\rho_2) \prod_{i_{k\sigma}i'_{ns}j_{ns}j'_{k\sigma}}^M}{(I_k - A_{\rho_1} - g_{k\rho_1})(I_k - A_{\rho_2} - g_{k\rho_2})} \right.
$$

$$
\left. + \sum_{\rho_1,\rho_2 \in ImO_R(N_R-1)} \frac{D_{pp'qq'}^{\sigma\sigma ss}(\rho_1\rho_2) \prod_{i'_{ns}i_{k\sigma}j'_{k\sigma}j_{ns}}^M}{(I_{\rho_1} - A_k - g_{\rho_1 k})(I_{\rho_2} - A_k - g_{\rho_2 k})} \right] - \sum_{\substack{pp' \in R \\ qq' \in R}} \sum_{ii'jj' \in \{r,l\}} \sum_{\sigma s} v_{pi_k} v_{p'i'_n} v_{qj_k} v_{q'j'_n} (-1)^{\delta_{\sigma s}}
$$

$$
\times \left[\sum_{\substack{\rho_1 \in ImO_R(N_R+1) \\ \rho_2 \in ImO_R(N_R-1)}} \frac{B_{pp'qq'}^{\sigma\sigma ss}(\rho_1\rho_2) \prod_{i_{k\sigma}i'_{ns}j'_{ns}j_{k\sigma}}^M}{(I_k - A_{\rho_1} - g_{k\rho_1})(I_{\rho_2} - A_n - g_{\rho_2 n})} + \sum_{\substack{\rho_1 \in ImO_R(N_R-1) \\ \rho_2 \in ImO_R(N_R+1)}} \frac{C_{pp'qq'}^{\sigma\sigma ss}(\rho_1\rho_2) \prod_{i'_{ns}i_{k\sigma}j_{k\sigma}j'_{ns}}^M}{(I_{\rho_1} - A_k - g_{\rho_1 k})(I_n - A_{\rho_2} - g_{n\rho_2})} \right],
$$

$$\tag{67}$$

The next contribution to the effective Hamiltonian for the R-subsystem is a c-number. The operator $\mathscr{V}^R$ can be written as

$$\mathscr{V}^R = - \sum_{mm' \in M} \sum_\sigma m_\sigma^+ m'_\sigma \sum_{B \in R} V_B^{mm'} Z_B^R$$

$$\approx - \sum_{A \in M} \sum_{m \in A \cap M} \sum_\sigma m_\sigma^+ m_\sigma \sum_{\substack{B \in R \\ B \neq A}} \gamma_{AB} Z_B^R \qquad (68)$$

Respective contribution is

$$\langle \Phi_{00}^M | P \mathscr{V}^R P \mathscr{2R}(0) \mathscr{2} P \mathscr{V}^R P | \Phi_{00}^M \rangle$$

$$= \sum_{\sigma\tau} \sum_{kn \in M} \sum_{ii'jj' \in \{r,l\}} \sum_{BB' \in R} V_B^{i_k i'_n} V_{B'}^{j_n j'_k} Z_B^R Z_{B'}^R \prod_{i_{k\sigma} i'_{n\sigma} j_{n\tau} j'_{k\tau}}^M$$

$$\approx \sum_{\sigma\tau} \sum_{k \in M} \prod_{r_{k\sigma} r_{k\sigma} r_{k\tau} r_{k\tau}}^M \sum_{BB' \in R} Z_B^R Z_{B'}^R ((1 - \delta_{BA_k}) \gamma_{BA_k}$$

$$- (1 - \delta_{BB_k}) \gamma_{BB_k})((1 - \delta_{B'A_k}) \gamma_{B'A_k}$$

$$- (1 - \delta_{B'B_k}) \gamma_{B'B_k}). \qquad (69)$$

From this approximate expression we can portion out the contribution which includes $BB' \notin \{A_k, B_k\}$:

$$\sum_{\sigma\tau} \sum_{k \in M} \prod_{r_{k\sigma} r_{k\sigma} r_{k\tau} r_{k\tau}}^M$$

$$\times \sum_{\substack{BB' \in R \\ BB' \notin \{A_k, B_k\}}} Z_B^R Z_{B'}^R (\gamma_{BA_k} - \gamma_{BB_k})(\gamma_{B'A_k} - \gamma_{B'B_k}). \qquad (70)$$

This contribution can be expressed through the bond polarizabilities. The two center integrals γ_{AB} can be approximated by their values calculated at the center of the kth bond with the corrections linear in interatomic vectors:

$$\gamma_{BA_k} = e(V(\mathbf{R}_B^{(k)}) - \tfrac{1}{2}(\nabla V(\mathbf{R}_B^{(k)}) \mathbf{R}_{A_k B_k})), \qquad (71)$$

where $V(\mathbf{R}_B^{(k)})$ is the potential induced by a unit charge placed on the atom B at the center of the kth bond; the correction contains the gradient of this potential. Substituting these expressions into Eq. (70), we get:

$$\sum_{\sigma\tau} \sum_{\substack{BB' \in R \\ BB' \notin \{A_k, B_k\}}} Z_B^R Z_{B'}^R \sum_{k \in M} (\nabla V(R_B^{(k)}) \mu_{A_k B_k}^{(k)})$$

$$\times (\nabla V(R_{B'}^{(k)}) \mu_{A_k B_k}^{(k)}) \prod_{r_{k\sigma} r_{k\sigma} r_{k\tau} r_{k\tau}}^M$$

$$= - \sum_{\substack{BB' \in R \\ BB' \notin \{A_k, B_k\}}} Z_B^R Z_{B'}^R$$

$$\times \sum_{k \in M} (\nabla V(R_{B'}^{(k)}) | \hat{\alpha}^{(k)}(0) | \nabla V(R_B^{(k)})), \qquad (72)$$

where the standard expressions reviewed in Ref. [20] for the bond polarizability tensors $\hat{\alpha}^{(k)}(\omega)$ for the kth bond through the polarization propagator for the corresponding geminal and the bond dipole vector $\mu_{A_k B_k}^{(k)}$ of the kth bond. The bond polarizabilities $\hat{\alpha}^{(k)}(0)$ are tabulated, for example, in Ref. [21].

The cross-term between the PV^cP and $PV^{rr}P$ is a sum of one-geminal and two-geminal contributions:

$$\langle \Phi_{00}^M | PV^c P \mathscr{2R}(0) \mathscr{2} PV^{rr} P | \Phi_{00}^M \rangle$$

$$= \sum_k \langle \Phi_{00}^M | PV^c P \mathscr{2R}(0) \mathscr{2} PV^{rr} P | \Phi_{00}^M \rangle_k$$

$$+ \sum_{k \neq n} \langle \Phi_{00}^M | PV^c P \mathscr{2R}(0) \mathscr{2} PV^{rr} P | \Phi_{00}^M \rangle_{kn}. \qquad (73)$$

The one-geminal contribution equals to

$$\langle \Phi_{00}^M | PV^c P \mathscr{Q}\mathscr{R}(0)\mathscr{Q}PV^{\pi\pi}P | \Phi_{00}^M \rangle_k$$

$$= \sum_{\substack{pp'\in R \\ qq'\in R}} \sum_{\substack{ii'jj'\in\{r,l\} \\ f\in\{a,b\}}} \sum_{\sigma\sigma'\tau} v_{qj_k} v_{q'j'_k} \left[\sum_{\rho_1\in Im O_R(N_R+1)} \frac{F_{pp'qq'}^{\sigma\sigma\tau\tau}(\rho_1)((pp'|i_k i'_k) - \delta_{\sigma\sigma'}(pi'_k|i_k p'))\Omega_{i_{k\sigma'}i'_{k\sigma'}j_{k\tau}j'_{k\tau}}^{f_{k-\tau}}}{(I_{kf} - A_{\rho_1} - g_{f_k\rho_1})} \right.$$

$$- \sum_{\rho_1\in Im O_R(N_R+1)} \frac{\delta_{\sigma\sigma'}\delta_{\sigma\tau} F_{pp'qq'}^{\sigma-\sigma-\sigma\sigma}(\rho_1)(pi'_k|i_k p')\Omega_{i_{k-\sigma}i'_{k\sigma}j_{k\sigma}j'_{k-\sigma}}^{f_{k\sigma}}}{(I_{kf} - A_{\rho_1} - g_{f_k\rho_1})}$$

$$- \sum_{\rho_1\in Im O_R(N_R-1)} (-1)^{\delta_{jj'}} \frac{G_{pp'qq'}^{\sigma\sigma\tau\tau}(\rho_1)((pp'|i_k i'_k) - \delta_{\sigma\sigma'}(pi'_k|i_k p'))\Omega_{i_{k\sigma'}i'_{k\sigma'}\tilde{j}_k\tilde{j}'_{k\tau}}^{f_{k-\tau}}}{(I_{\rho_1} - A_{kf} - g_{\rho_1 f_k})}$$

$$- \sum_{\rho_1\in Im O_R(N_R-1)} (-1)^{\delta_{jj'}} \frac{\delta_{\sigma\sigma'}\sigma_{\sigma\tau}G_{pp'qq'}^{\sigma-\sigma-\sigma\sigma}(\rho_1)(pi'_k|i_k p')\Omega_{i_{k-\sigma}i'_{k\sigma}\tilde{j}_{k\sigma}k-\sigma_{j'}}^{f_{k\sigma}}}{(I_{\rho_1} - A_{kf} - g_{\rho_1 f_k})} \right], \tag{74}$$

while the two-geminal contribution is

$$\langle \Phi_{00}^M | PV^c P \mathscr{Q}\mathscr{R}(0)\mathscr{Q}PV^{\pi\pi}P | \Phi_{00}^M \rangle_{kn}$$

$$= \sum_{\substack{pp'\in R \\ qq'\in R}} \sum_{\substack{ii'jj'\in\{r,l\} \\ f\in P\{a,b\}}} \sum_{\sigma\tau} \sum_{\rho_1\in Im O_R(N_R+1)} v_{qj_n} v_{q'j'_k} \left[\frac{F_{pp'qq'}^{\sigma\sigma\tau\tau}(\rho_1)((pp'|i_k i'_n) - \delta_{\sigma\tau}(pi'_n|i_k p'))\Omega_{i_{k\tau}i'_{n\tau}j_{n\tau}j'_{k\tau}}^{f_{k-\tau}}}{(I_{kf} - A_{\rho_1} - g_{f_k\rho_1})} \right.$$

$$\left. - \frac{\delta_{\sigma\tau} F_{pp'qq'}^{\sigma-\sigma-\sigma\sigma}(\rho_1)(pi'_n|i_k p')\Omega_{i_{k-\sigma}i'_{n\sigma}j_{n\sigma}j'_{k-\sigma}}^{f_{k\sigma}}}{(I_{kf} - A_{\rho_1} - g_{f_k\rho_1})} \right]$$

$$- \sum_{\substack{pp'\in R \\ qq'\in R}} \sum_{\substack{ii'jj'\in\{r,l\} \\ f\in\{a,b\}}} \sum_{\sigma\tau} \sum_{\rho_1\in Im O_R(N_R-1)} v_{qj_k} v_{q'j'_n} \left[\frac{G_{pp'qq'}^{\sigma\sigma\tau\tau}(\rho_1)((pp'|i_k i'_n) - \delta_{\sigma\tau}(pi'_n|i_k p'))\Omega_{i_{k\tau}i'_{n\tau}j'_{n\tau}j_{k\tau}}^{f_{n-\tau}}}{(I_{\rho_1} - A_{nf} - g_{\rho_1 f_n})} \right.$$

$$\left. - \frac{\delta_{\sigma\tau}G_{pp'qq'}^{\sigma-\sigma-\sigma\sigma}(\rho_1)(pi'_n|i_k p')\Omega_{i_{k-\sigma}i'_{n\sigma}j'_{n\sigma}j_{k-\sigma}}^{f_{n-\sigma}}}{(I_{\rho_1} - A_{nf} - g_{\rho_1 f_n})} \right], \tag{75}$$

where the operator multipliers are:

$$F_{pp'qq'}^{\sigma\sigma'\tau\tau'}(\rho_1) = p_\sigma^+ p'_{\sigma'}(1 - |0_R\rangle\langle 0_R|)q_\tau|\rho_1\rangle\langle\rho_1|q'^+_{\tau'}, \qquad G_{pp'qq'}^{\sigma\sigma'\tau\tau'}(\rho_1) = p_\sigma^+ p'_{\sigma'}(1 - |0_R\rangle\langle 0_R|)q_\tau^+|\rho_1\rangle\langle\rho_1|q'_{\tau'}, \tag{76}$$

and new quantity which is somewhat intermediate between Π and Ξ is introduced:

$$\Omega^{f}_{ii'jj'} = -\sum_{\mu \neq 0} \frac{\langle \Phi^{M}_{00}|i^{+}i'|\mu\rangle\langle\mu|j^{+}f^{+}fj'|\Phi^{M}_{00}\rangle}{\epsilon_{\mu}}. \quad (77)$$

All the excited states, their relative energies and matrix averages are determined above. As for the Ξs, the summation over upper indices of the Ωs gives the polarization propagator. Therefore, assuming that ionization energies for the different BOs of the kth geminal are equal, we obtain

$$\langle \Phi^{M}_{00}|PV^{c}P\mathscr{2R}(0)\mathscr{2}PV^{rr}P|\Phi^{M}_{00}\rangle_{k}$$

$$= \sum_{\substack{pp'\in R \\ qq'\in R}} \sum_{ii'jj'\in\{r,l\}} \sum_{\sigma\sigma'\tau} v_{qj_k}v_{q'j'_k} \left[\sum_{\rho_1\in Im O_R(N_R+1)} \frac{F^{\sigma\sigma'\tau\tau}_{pp'qq'}(\rho_1)((pp'|i_k i'_k) - \delta_{\sigma\sigma'}(pi'_k|i_k p'))\prod^{M}_{i_{k\sigma'}i'_{k\sigma'}j_{k\tau}j'_{k\tau}}}{(I_k - A_{\rho_1} - g_{k\rho_1})} \right.$$

$$- \sum_{\rho_1\in Im O_R(N_R+1)} \frac{\delta_{\sigma\sigma'}\delta_{\sigma\tau}F^{\sigma-\sigma-\sigma\sigma}_{pp'qq'}(\rho_1)(pi'_k|i_k p')\prod^{M}_{i_{k-\sigma}i'_{k\sigma}j_{k\sigma}j'_{k-\sigma}}}{(I_k - A_{\rho_1} - g_{k\rho_1})}$$

$$- \sum_{\rho_1\in Im O_R(N_R-1)} (-1)^{\delta_{jj'}} \frac{G^{\sigma\sigma'\tau\tau}_{pp'qq'}(\rho_1)((pp'|i_k i'_k) - \delta_{\sigma\sigma'}(pi'_k|i_k p'))\prod^{M}_{i_{k\sigma'}i'_{k\sigma'}\tilde{j}_{k\tau}\tilde{j}'_{k\tau}}}{(I_{\rho_1} - A_k - g_{\rho_1 k})}$$

$$\left. - \sum_{\rho_1\in Im O_R(N_R-1)} (-1)^{\delta_{jj'}} \frac{\delta_{\sigma\sigma'}\delta_{\sigma\tau}G^{\sigma-\sigma-\sigma\sigma}_{pp'qq'}(\rho_1)(pi'_k|i_k p')\prod^{M}_{i_{k-\sigma}i'_{k\sigma}\tilde{j}_{k\sigma}\tilde{j}'_{k-\sigma}}}{(I_{\rho_1} - A_k - g_{\rho_1 k})} \right], \quad (78)$$

for the one-geminal contributions and

$$\langle \Phi^{M}_{00}|PV^{c}P\mathscr{2R}(0)\mathscr{2}PV^{rr}P|\Phi^{M}_{00}\rangle_{kn}$$

$$= \sum_{\substack{pp'\in R \\ qq'\in R}} \sum_{ii'jj'\in\{r,l\}} \sum_{\sigma\tau} \sum_{\rho_1\in Im O_R(N_{R+1})} v_{qj_n}v_{q'j'_k} \left[\frac{F^{\sigma\sigma\tau\tau}_{pp'qq'}(\rho_1)((pp'|i_k i'_n) - \delta_{\sigma\tau}(pi'_n|i_k p'))\prod^{M}_{i_{k\tau}i'_{n\tau}j_{n\tau}j'_{k\tau}}}{(I_k - A_{\rho_1} - g_{k\rho_1})} \right.$$

$$\left. - \frac{\delta_{\sigma\tau}F^{\sigma-\sigma-\sigma\sigma}_{pp'qq'}(\rho_1)(pi'_n|i_k p')\prod^{M}_{i_{k-\sigma}i'_{n\sigma}j_{n\sigma}j'_{k-\sigma}}}{(I_k - A_{\rho_1} - g_{k\rho_1})} \right] - \sum_{\substack{pp'\in R \\ qq'\in R}} \sum_{ii'jj'\in\{r,l\}} \sum_{\sigma\tau} \sum_{\rho_1\in Im O_R(N_R-1)} v_{qj_k}v_{q'j'_n}$$

$$\times \left[\frac{G^{\sigma\sigma\tau\tau}_{pp'qq'}(\rho_1)((pp'|i_k i'_n) - \delta_{\sigma\tau}(pi'_n|i_k p'))\prod^{M}_{i_{k\tau}i'_{n\tau}j_{n\tau}j_{k\tau}}}{(I_{\rho_1} - A_n - g_{\rho_1 n})} - \frac{\delta_{\sigma\tau}G^{\sigma-\sigma-\sigma\sigma}_{pp'qq'}(\rho_1)(pi'_n|i_k p')\prod^{M}_{i_{k-\sigma}i'_{n\sigma}j_{n\sigma}j_{k-\sigma}}}{(I_{\rho_1} - A_n - g_{\rho_1 n})} \right], \quad (79)$$

for the two-geminal contributions.

The cross-term between the PV^cP and $P\mathscr{V}^RP$ equals

$$\langle\Phi_{00}^M|PV^cP\mathscr{2R}(0)\mathscr{2}P\mathscr{V}^RP|\Phi_{00}^M\rangle$$

$$= -\sum_{pp'\in R}\sum_{B\in R}Z_B^R\sum_{\sigma\sigma'\tau}p_\sigma^+ p'_\sigma(1$$

$$-|0_R\rangle\langle 0_R|)\sum_{kn\in M}\sum_{ii'jj'\in\{r,l\}}((pp'|i_ki'_n)$$

$$-\delta_{\sigma\sigma'}(pi'_n|i_kp'))V_B^{j_nj'_k}\prod_{i_{k\sigma'}i'_{n\sigma'}j_{n\tau}j'_{k\tau}}^M. \quad (80)$$

In the case when the ZDO approximation is employed for the two-electron integrals, we have:

$$\langle\Phi_{00}^M|PV^cP\mathscr{2R}(0)\mathscr{2}P\mathscr{V}^RP|\Phi_{00}^M\rangle$$

$$= -\sum_{p\in R}\sum_{B\in R}Z_B^R\sum_{k\in M}\sum_{i\in\{r,l\}}\sum_{\sigma\tau'}p_\sigma^+ p_\sigma(1-|0_R\rangle\langle 0_R|)$$

$$\times((pp|i_ki_k)-\delta_{\sigma\sigma'}(pi_k|i_kp))(\gamma_{BA_k}-\gamma_{BB_k})\prod_{i_{k\sigma'}i_{k\sigma'}r_{k\tau}r_{k\tau}}^M. \quad (81)$$

The cross-term between $PV^{rr}P$ and $P\mathscr{V}^RP$ equals

$$\langle\Phi_{00}^M|P\mathscr{V}^RP\mathscr{2R}(0)\mathscr{2}PV^{rr}P|\Phi_{00}^M\rangle$$

$$= \sum_k\langle\Phi_{00}^M|P\mathscr{V}^RP\mathscr{2R}(0)\mathscr{2}PV^{rr}P|\Phi_{00}^M\rangle_k$$

$$+ \sum_{k\neq n}\langle\Phi_{00}^M|P\mathscr{V}^RP\mathscr{2R}(0)\mathscr{2}PV^{rr}P|\Phi_{00}^M\rangle_{kn}. \quad (82)$$

The one-geminal contribution equals

$$\langle\Phi_{00}^M|P\mathscr{V}^RP\mathscr{2R}(0)\mathscr{2}PV^{rr}P|\Phi_{00}^M\rangle_k$$

$$= -\sum_{pp'\in R}\sum_{\sigma\tau}\sum_{\substack{ii'jj'\in\{r,l\}\\f\in\{a,b\}}}\sum_{B\in R}Z_B^R V_B^{i_ki'_k}v_{pj_k}v_{p'j'_k}(1-|0_R\rangle\langle 0_R|)$$

$$\times\Bigg[\sum_{\rho_1\in ImO_R(N_R+1)}\frac{p_\tau|\rho_1\rangle\langle\rho_1|p'_\tau++\Omega_{i_{k\sigma}i'_{k\sigma}j_{k\tau}j'_{k\tau}}^{f_{k-\tau}}}{I_{kf}-A_{\rho_1}-g_{f_k\rho_1}}$$

$$-\sum_{\rho_1\in ImO_R(N_R-1)}(-1)^{\delta_{jj'}}\frac{p_\tau^+|\rho_1\rangle\langle\rho_1|p'_\tau\Omega_{i_{k\sigma}i'_{k\sigma}\tilde{j}_{k\tau}\tilde{j}'_{k\tau}}^{f_{k-\tau}}}{I_{\rho_1}-A_{kf}-g_{\rho_1 f_k}}\Bigg], \quad (83)$$

while the two-geminal contribution equals

$$\langle\Phi_{00}^M|P\mathscr{V}^RP\mathscr{2R}(0)\mathscr{2}PV^{rr}P|\Phi_{00}^M\rangle_{kn}$$

$$= -\sum_{pp'\in R}\sum_\sigma\sum_{\substack{ii'jj'\in\{r,l\}\\f\in\{a,b\}}}\sum_{B\in R}Z_B^R V_B^{i_ki'_n}(1-|0_R\rangle\langle 0_R|)$$

$$\times\Bigg[\sum_{\rho_1\in ImO_R(N_R+1)}\frac{p_\sigma|\rho_1\rangle\langle\rho_1|p'^+_\sigma\Omega_{i_{k\sigma}i'_{n\sigma}j_{n\sigma}j'_{k\sigma}}^{f_{k-\sigma}}v_{pj_n}v_{p'j'_k}}{I_{kf}-A_{\rho_1}-g_{f_k\rho_1}}$$

$$-\sum_{\rho_1\in ImO_R(N_R-1)}(-1)^{\delta_{jj'}}\frac{p_\sigma^+|\rho_1\rangle\langle\rho_1|p'_\sigma\Omega_{i_{k\sigma}i'_{n\sigma}j'_{n\sigma}j_{k\sigma}}^{f_{n-\sigma}}v_{pj_k}v_{p'j'_n}}{I_{\rho_1}-A_{nf}-g_{\rho_1 f_n}}\Bigg]. \quad (84)$$

This term, in the case when the ZDO approximation is used for two-electron integrals, equals:

$$\langle\Phi_{00}^M|P\mathscr{V}^RP\mathscr{2R}(0)\mathscr{2}PV^{rr}P|\Phi_{00}^M\rangle$$

$$= -\sum_{pq\in R}\sum_{B\in R}Z_B^R(1-|0_R\rangle\langle 0_R|)\sum_{k\in M}\sum_{\substack{jj'\in\{r,l\}\\f\in\{a,b\}}}\sum_{\sigma\tau}v_{pj_k}v_{qj'_k}$$

$$\times\Bigg[\sum_{\rho_1\in ImO_R(N_R+1)}\frac{\sum_\sigma p_\tau|\rho_1\rangle\langle\rho_1|q_\tau^+(\gamma_{BA_k}\Omega_{r_{k\sigma}r_{k\sigma}j_{k\tau}j'_{k\tau}}^{f_{k-\tau}}+\gamma_{BB_k}\Omega_{l_{k\sigma}l_{k\sigma}j_{k\tau}j_{k\tau}}^{f_{k-\tau}})}{I_{kf}-A_{\rho_1}-g_{f_k\rho_1}}$$

$$-\sum_{\rho_1\in ImO_R(N_R-1)}(-1)^{\delta_{jj'}}\frac{\sum_\sigma p_\tau^+|\rho_1\rangle\langle\rho_1|q_\tau(\gamma_{BA_k}\Omega_{r_{k\sigma}r_{k\sigma}\tilde{j}_{k\tau}\tilde{j}'_{k\tau}}^{f_{k-\tau}}+\gamma_{BB_k}\Omega_{l_{k\sigma}l_{k\sigma}\tilde{j}_{k\tau}\tilde{j}'_{k\tau}}^{f_{k-\tau}})}{I_{\rho_1}-A_{kf}-g_{\rho_1 f_k}}\Bigg]. \quad (85)$$

If the energies of electron transfer from (or to) the kth geminal do not depend on the type of ionized orbital, we obtain that the Eq. (85) transforms to

$$
\langle \Phi_{00}^M | P \mathscr{V}^R P \mathscr{2R}(\omega) \mathscr{2} P V^{rr} P | \Phi_{00}^M \rangle
$$

$$
= - \sum_{pq \in R} \sum_{B \in R} Z_B^R (1 - |0_R\rangle\langle 0_R|) \sum_{k \in M} \sum_{jj' \in \{r,l\}} \sum_{\sigma\tau} v_{pj_k} v_{qj_k'}
$$

$$
\times \left[\sum_{\rho_1 \in ImO_R(N_R + 1)} \frac{\sum_\sigma p_\tau |\rho_1\rangle\langle\rho_1|q_\tau^+ \left(\gamma_{BA_k} \prod_{r_{k\sigma} r_{k\sigma} j_{k\tau} j_{k\tau}'}^M + \gamma_{BB_k} \prod_{l_{k\sigma} l_{k\sigma} j_{k\tau} j_{k\tau}'}^M \right)}{I_k - A_{\rho_1} - g_{k\rho_1}} \right.
$$

$$
\left. - \sum_{\rho_1 \in ImO_R(N_R - 1)} (-1)^{\delta_{jj'}} \frac{\sum_\sigma p_\tau^+ |\rho_1\rangle\langle\rho_1|q_\tau \left(\gamma_{BA_k} \prod_{r_{k\sigma} r_{k\sigma} \tilde{j}_{k\tau} \tilde{j}_{k\tau}'}^M + \gamma_{BB_k} \prod_{l_{k\sigma} l_{k\sigma} \tilde{j}_{k\tau} \tilde{j}_{k\tau}'}^M \right)}{I_{\rho_1} - A_k - g_{\rho_1 k}} \right].
$$

$$(86)$$

The last contribution to the effective Hamiltonian of the quantum subsystem is a c-number and can be written as

$$
\langle \Phi_{00}^M | P \mathscr{V}^R P | \Phi_{00}^M \rangle = -2 \sum_{\substack{A \in M \\ }} \sum_{\substack{B \in R \\ B \neq A}} \gamma_{AB} Z_B^R \sum_{\substack{t_n \in A \\ n \in M}} P_n^{tt}. \quad (87)
$$

Thereby, we obtained the explicit form of the effective Hamiltonian for the R-subsystem. It allows not only to determine the wave function of the R-subsystem but also to obtain the electronic energy of the whole molecule, which can be written [11] as

$$
\mathscr{E}_0(q) = E_0^R(q) + E_{00}^M(q),
$$

where $E_0^R(q)$ is the lowest eigenvalue of the effective Hamiltonian Eq. (6) of the R-subsystem and $E_{00}^M(q)$ is the energy of the M-subsystem which is parametrized in the MM form (The detailed transition from the local QM description of molecular electronic structure to the MM will be published elsewhere [17]).

To demonstrate the importance of transition from the bare Hamiltonian for the R-subsystem to its effective Hamiltonian we have estimated using the above formulae the renormalization of the two-electron parameters of Coulomb interaction (γ_{11} and γ_{12}) in the PPP Hamiltonian due to interaction of the π-system with the σ-core. In fact the $\sigma-\pi$-separation is one of the first examples of separation of electron

variables. Incidentally, in this case the contribution of the intersubsystem resonance vanishes for the symmetry reasons. We want to emphasize that the values of correction are independent on the bare values of parameters. We start from the bare value of $\sim$7.6 eV for the γ_{12} parameter for the double C–C bond calculated by the formulae accepted in the standard MINDO/3 method and the bare value of $\sim$11.8 eV for the γ_{11} parameter which is obtained from atomic spectra [22]. We accepted the bond length value 1.339 Å which corresponds to that in ethylene. The correction to the γ_{11} and γ_{12} parameters is due to the contribution Eq. (37) to the effective Hamiltonian only. In fact, in the ethylene molecule, the geminals corresponding to the C–C and C–H bonds contribute to the correction. The numeric estimate of the correction to γ_{11} is negative (the renormalized γ_{11} is smaller than its bare value) and equals to $\sim$0.45 eV. This value is not very large which justifies the application of the perturbation theory to correct the bare Hamiltonian. At the same time, this value suffices to be important for constructing the Hamiltonian for the π-subsystem. Also, we obtained that the normalization of the γ_{12} parameter is very small (less than 0.3%) and thus can be neglected.

3. Discussion

The QM/MM methods become more and more popular in theoretical modeling of large molecular

systems. It is caused by rapidly growing needs of bio-
logical and organometallic chemistry. The application
of the QM/MM schemes to calculations on molecular
electronic structure and chemical reactivity is very
advantageous. However, the results of up-to-day
QM/MM calculations depend on the form of the junc-
tion between QM and MM subsystems and, therefore,
are ambiguous. All the junction forms proposed in the
literature are empirical. It seems to be important to
substantiate the form of the junction on the basis of
quantum chemical consideration of interaction
between the parts of the molecular system, treated
on the quantum and classical level. In the present
work, we performed a sequential derivation of the
hybrid QM/MM scheme on the basis of a previously
developed local description of molecular electronic
structure [15,16]. This allows to express finally the
renormalizations of the bare Hamiltonian in terms of
the local quantities characterizing the two-electron
bonds in the chemically inert, i.e. classical subsystem,
which can be either calculated or estimated from
experimental data on the bond polarizabilities [21].

In order to construct the effective Hamiltonian for
the quantum system or equivalently the QM/MM
junction, we have taken into account both electron
transfers between the subsystems and the excitations
in the classical part of the molecular system. We have
obtained the explicit expressions for this renormaliza-
tion, which is the function of well-defined character-
istics like the polarization propagators of the *M*-
subsystem. Our consideration also required to intro-
duce new quantities Ξ and Ω which appear due to
entanglements of one-electron transfers between the
subsystems and excitations leaving the number of
electrons in two subsystems unchanged. If the ener-
gies of the states with one-electron transfers between
the two subsystems are replaced with an average
value, the quantities Ξ and Ω in the expressions for
the effective Hamiltonian for the quantum subsystem
are reduced to the polarization propagators. This
allows us to express the contributions renormalizing
the Coulomb interaction of electrons in the quantum
part of the system through such observable quantities
as the bond polarizabilities are. The same applies to
the corrections renormalizing the one-electron terms
of the Hamiltonian for the quantum part. The possibi-
lity to express the corrections to the Hamiltonian for
the *R*-subsystem through the experimentally observa-

ble quantities such as bond polarizabilities and the
ionization potentials of the bonds allows us to elim-
inate the calculations of the electronic structure of the
classical part of the whole molecular system and to
parameterize them. The above reduction of the QM/
MM junction to the sum of transferable contributions
from the chemical bonds remaining in the classical
part was possible due to the special form for the impli-
cit wave function of electrons underlying the descrip-
tion of the classical part of the system with use of the
MM type schemes. We use the APSLG form for this
wave function. This provides a route to a possible
derivation of the classical (MM) description of the
M-subsystem.

With use of the formulae derived above for the
effective Hamiltonian for the quantum subsystem,
we addressed the old problem of substantiation of
the parameters of the PPP Hamiltonian (see, for
example, Ref. [23]). The PPP Hamiltonian for the
π-electrons is historically one of the earliest examples
of successful separation of electron variables with
those in the π-subsystem treated on the QM level,
while those in the σ-subsystem left to a classical (in
fact, MM-like) description. The value of parameter
γ_{11} in the PPP Hamiltonian equals to 11.1 eV (the
numerical values of parameters vary by about
0.5 eV in different works on the π-Hamiltonian).
The value obtained from atomic spectra of carbon
[22] is larger by $\sim$0.7 eV. This value is effective
and implicitly includes the multiparticle corrections
[22,24] which appear due to reduction of the complete
one-electron basis to the valence one. The difference
between the PPP and experimentally estimated atomic
values can be explained by the influence of the σ-core
on the π-subsystem. The correction value (0.45 eV)
obtained using the formulae written above and the
MINDO/3 approximation for the molecular integrals
is smaller than the required value of 0.7 eV by abso-
lute value but the sign (negative) and the order of
magnitude for this increment are correct. The bare
value of the γ_{12} parameter strongly depends on the
type of approximation. The correction to this value
is small (see above). In Ref. [24], an attempt to obtain
the corrections to π-Hamiltonian of benzene from the
σ-core is mentioned. The result is a very small correc-
tion to the γ_{12} parameter which is in accordance with
our result. However, the correction to the γ_{11} para-
meter is positive and exceeds 1.2 eV. Thus the value

of the γ_{11} parameter obtained in that work is by 10% larger than the PPP one. Moreover, the positive sign of the correction contradicts the physical picture of screening of electronic interactions in the π-subsystem due to interaction with the polarization fluctuations in the σ-subsystem (see, for example, Ref. [25]). More advanced attempt to obtain parameters of the π-electron Hamiltonian was made in Ref. [26] by using the ab initio effective valence shell Hamiltonian formalism. Starting from the ab initio Hamiltonian, the parameters of π-Hamiltonian were estimated perturbatively. The value of the parameter γ_{12} was obtained to be ~ 7.8 eV that is close to the value of the PPP Hamiltonian. However, also in Ref. [26] the value of the parameter γ_{11} was obtained to be ~ 12 eV. This is significantly larger than the value of the PPP Hamiltonian (which is sufficiently well established from the experimental data) and is close to the value obtained from analysis of the excitation spectra of free carbon atoms and ions [22]. Therefore, we conclude that the screening of electronic interactions due to σ-core can be estimated with use of the formalism introduced in the present paper. It noticeably reduces the value of the one-center electron–electron repulsion γ_{11} parameter obtained from the atomic spectra, but the correction to the two-center electron–electron repulsion γ_{12} parameters is negligibly small.

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