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Effective Hamiltonian for conjugated polyenes based on the ground state single-electron density matrix

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Abstract

A method for constructing effective Hamiltonians using the information contained in the ground state reduced single-electron density matrices for many-electron systems is proposed and applied to trans-polyacetylene oligomers $C_{2n}H_{2n+2}$ with $n = 4-24$. The resulting effective Hamiltonians for π electrons, expanded in the basis set of natural atomic orbitals (NAOs) with nearest neighbor transfer integrals, reproduce accurately the Hartree–Fock ground state density matrices.

Despite the tremendous progress in quantum chemistry, *ab initio* calculations of electronic structure are still limited to relatively small sizes. Realistic modeling of very large systems requires a reduced description using effective Hamiltonians. Pseudopotentials and effective core potentials have been employed to replace the core electrons [1–4]. Pariser, Parr, and Pople have developed a systematic procedure for determining effective Hamiltonians of conjugated organic molecules [5–8]. This semi-empirical procedure requires experimental input in the parameterization. Using a formalism developed by Brandow [9], Freed and co-workers implemented a rigorous procedure to determine effective Hamiltonians for single- and multi-atom systems [10]. This procedure requires the evaluation of complex operators, and is thus limited for small systems such as butadiene, benzene and hexatriene.

In this Letter we propose a procedure for con-

structing an effective Hamiltonian by using the ground state reduced single-electron density matrix, the form of electron–electron effective Coulomb interaction, and the optical gap. The reduced density matrix is obtained from *ab initio* quantum chemistry calculations. The Coulomb interaction among the valence and conduction electrons can be inferred from many-body theory. Since the electronic charge distributions and bond orders which characterize the density matrix are local quantities, the effective Hamiltonian should converge rapidly with size, and this makes accurate calculations possible for very large systems by making use of *ab initio* calculations on smaller systems. In addition, the effective Hamiltonian makes it possible to predict electronic excitations and corresponding linear and nonlinear optical spectra using ground state information, which is much more readily available than excited state energies and wavefunctions [11].

We assume the following form for the effective Hamiltonian of a many-electron system

$$H'_0 = H_e + H_{ee},$$

$$H_e = \sum_{mn} t_{mn} a_m^+ a_n,$$

$$H_{ee} = \sum_{mn} V_{mn} a_m^+ a_n^+ a_n,$$

where $a_m^+(a_n)$ is an electron creation (annihilation) operator at a localized basis orbital $m(n)$. t_{mn} is the transfer integral between orbitals m and n , and V_{mn} is the electron–electron effective Coulomb interaction. Here we employ the zero differential overlap approximation assuming localized basis orbitals [5,6]. The Hartree–Fock ground state reduced single-electron density matrix ρ satisfies the equation $[h, \rho] = 0$, with the Fock matrix $h_{nm} = t_{nm} + 2\delta_{nm} \sum_l V_{nl} \rho_{ll} - V_{nm} \rho_{nm}$. This equation can be recasted in the form

$$f_{nm} \equiv \sum_k \rho_{kn} t_{mk} - \sum_k \rho_{mk} t_{kn} + R_{mn} = 0, \quad (1)$$

where

$$R_{mn} \equiv \sum_k (V_{mk} - V_{nk})(2\rho_{kk} \rho_{mn} - \rho_{mk} \rho_{kn}).$$

For a basis set of N orbitals, and when V_{nm} is given, Eq. (1) is a set of $D_i = N(N-1)/2$ linear equations for the same number of unknown t_{nm} (note that $t_{nm} = t_{mn}$). This may suggest that the effective Hamiltonian can be uniquely determined. However, the number of independent pieces of information contained in ρ , D_ρ , is less than D_i . This means that not all D_i linear equations are independent. To evaluate D_ρ of a half filled system with N molecular orbitals, we need to determine the coefficients of $N/2$ occupied molecular orbitals. This is equivalent to determining $N/2$ orthogonal unit vectors in an N -dimensional space. $N-1$ parameters are needed to determine the first molecular orbital, $N-2$ parameters are needed for the second one, and so on. Finally, $N/2$ parameters are needed for the last orbital. Thus, $D_\rho = (N-1) + (N-2) + \dots + N/2 = N(3N-2)/8 \leq D_i$. $\{t_{mn}\}$ can be determined by minimizing $\sum_{mn} f_{mn}^2$. In practice, additional constraints should be imposed on the system. For instance, symmetry usually requires certain relationships among $\{t_{mn}\}$, and physical arguments may allow us to set certain elements to zero. These con-

straints which restrict the possible values of $\{t_{mn}\}$ and confine the effective Hamiltonians to physical space, can be introduced variationally. We define

$$S(\{t_{mn}\}, \{V_{mn}\}, \{\rho_{mn}\}) = \sum_{mn} f_{mn}^2 + \mathcal{F}. \quad (2)$$

Here \mathcal{F} represents variational constraints. Upon minimizing $S(\{t_{mn}\}, \{V_{mn}\}, \{\rho_{mn}\})$ with respect to $\{t_{ij}\}$, we have

$$\frac{\partial S}{\partial t_{ij}} = 2 \sum_{mn} f_{mn} \frac{\partial f_{mn}}{\partial t_{ij}} + \frac{\partial \mathcal{F}}{\partial t_{ij}} = 0. \quad (3)$$

The effective Hamiltonian is determined by solving (3) for $\{t_{mn}\}$.

We have applied this procedure to polyacetylene chains $C_{2n}H_{2n+2}$ with $N = 2n = 8, 10, \dots, 48$. In these systems the carbon $2p\pi$ electrons are the valence electrons. Each localized π orbital is characterized by a site index i running from 1 to N . Polyacetylene has inversion symmetry. Thus, $t_{ij} = t_{\bar{i}\bar{j}}$ where $\bar{i} = N+1-i$ and $\bar{j} = N+1-j$. Since $t_{ij} = t_{ji}$, we consider only $i \geq j$. With $\mathcal{F} = 0$, Eq. (3) becomes,

$$\begin{aligned} & \sum_{mk} \rho_{km} \rho_{jm} t_{ik} + \sum_{mk} \rho_{km} \rho_{jm} t_{\bar{i}\bar{k}} + \sum_{mk} \rho_{km} \rho_{im} t_{jk} \\ & + \sum_{mk} \rho_{km} \rho_{\bar{i}\bar{m}} t_{\bar{j}\bar{k}} \\ & - \sum_{mk} (\rho_{ik} \rho_{jm} + \rho_{jk} \rho_{im} + \rho_{\bar{i}\bar{k}} \rho_{\bar{j}\bar{m}} + \rho_{\bar{j}\bar{k}} \rho_{\bar{i}\bar{m}}) t_{km} \\ & + \sum_m (R_{im} \rho_{jm} + R_{\bar{i}\bar{m}} \rho_{\bar{j}\bar{m}} + R_{jm} \rho_{im} + R_{\bar{j}\bar{m}} \rho_{\bar{i}\bar{m}}) \\ & = 0. \end{aligned} \quad (4)$$

Employing GAUSSIAN 94 with minimal basis set, we obtained Hartree–Fock ground states for $N = 2n = 8 \rightarrow 48$. Under the constraint that the lengths of different single or double bonds are equal, geometry optimization was employed for each molecule. Using these calculations we constructed the corresponding reduced single-electron density matrices in the basis set of the natural atomic orbitals (NAOs) [12]. The NAOs are the orthonormal atomic orbitals of maximal occupancy for a given wavefunction [13]. They diagonalize the atomic reduced single-electron density matrix, and thus provide an extremely compact representation of electron properties.

Table 1
Parameters of the effective PPP-like Hamiltonian for $N = 14$ (in eV)^a

	$i = 2$	$i = 3$	$i = 4$	$i = 5$	$i = 6$	$i = 7$	$i = 8$
$t_{i,i-1}$	-2.513	-1.801	-2.515	-1.791	-2.492	-1.781	-2.481
t_{ii}	-3.072	-5.269	-6.393	-7.238	-7.665	-7.903	-7.903
t_{ii}^* ^b	0.069	0.075	0.081	0.082	0.085	0.085	0.085
$t_{i,i-1}$	-2.514	-1.800	-2.513	-1.790	-2.490	-1.780	-2.478
t_{ii}^* ^b	0.0	0.0	0.003	0.003	0.004	0.004	0.004
$t_{i,i-2}$		-0.117	-0.120	-0.122	-0.123	-0.125	-0.124

^a Optimized single bond length $R_s = 1.48 \text{ \AA}$ and double bond length $R_d = 1.33 \text{ \AA}$; the upper panel assumes only the nearest neighbor transfer integrals, and lower panel includes also the next nearest neighbor transfer integrals.

^b t_{ii}^* is set to zero.

The Coulomb interaction is assumed to have the Ohno form [14,15],

$$V_{mn} = \frac{U}{[1 + (r_{mn}/a_0)^2]^{1/2}}, \quad (5)$$

where r_{mn} is the distance between sites m and n , $a_0 = e^2/U\epsilon$ describes the characteristic length of the effective Coulomb interaction, ϵ is the dielectric constant. U is the on-site Coulomb interaction. We may solve Eq. (4) for the scaled hopping elements $\tilde{t}_{ij} \equiv t_{ij}/U$ by assuming $a_0 = 1.0 \text{ \AA}$.

The transfer integrals between two atoms vary exponentially with internuclear distance. A reasonable approximation is to retain only the on-site and the nearest neighbor terms. Setting $\tilde{t}_{11} = 0$, Eq. (4)

becomes a set of $D_m = N - 1$ linear equations. First we solved \tilde{t}_{ij} for tetradecaheptaene ($N = 14$). Then the experimental optical gap is utilized to determine U . Sondheimer and co-workers measured absorption spectra of a series conjugated polyacetylenes in isoctane [16]. The optical gap of tetradecaheptaene is 3.18 eV. We have calculated the gap by employing the coupled-electronic-oscillator (CEO) technique [17,18]. This leads to $U = 6.64 \text{ eV}$. In Table 1 we list the resulting t_{ij} . Note that the hopping terms along either double or single bonds are very close. The average transfer integrals for double (t_d) and single bonds (t_s) are -2.50 and -1.79 eV , respectively.

To check the validity of our effective Hamiltonian, we have used it to compute the ground state

Table 2
Some elements of reduced single-electron density matrix ρ_{ij} ($i = 1 \rightarrow 7$ and $j = 1 \rightarrow 7$)^a

i	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$	$j = 6$	$j = 7$
1	0.505 (-4.76)	0.478 (-4.16)	-0.001 (-2.04)	-0.133 (-0.38)	0.000 (2.26)	0.055 (-0.32)	0.000 (-1.00)
2		0.496 (-3.21)	0.146 (-3.17)	0.002 (-3.41)	-0.018 (-0.60)	-0.001 (-2.03)	0.005 (-1.81)
3			0.501 (-4.62)	0.457 (-5.68)	0.000 (-1.26)	-0.128 (2.09)	0.000 (0.87)
4				0.499 (-5.45)	0.152 (0.20)	0.001 (4.00)	-0.020 (2.59)
5					0.500 (1.64)	0.455 (-0.95)	0.000 (-1.45)
6						0.499 (-4.10)	0.153 (-0.88)
7							0.500 (2.50)

^a The numbers in parentheses are the difference between the input density matrix elements from GAUSSIAN 94 calculation and those predicted by the effective Hamiltonian. They should be multiplied by 10^{-5} .

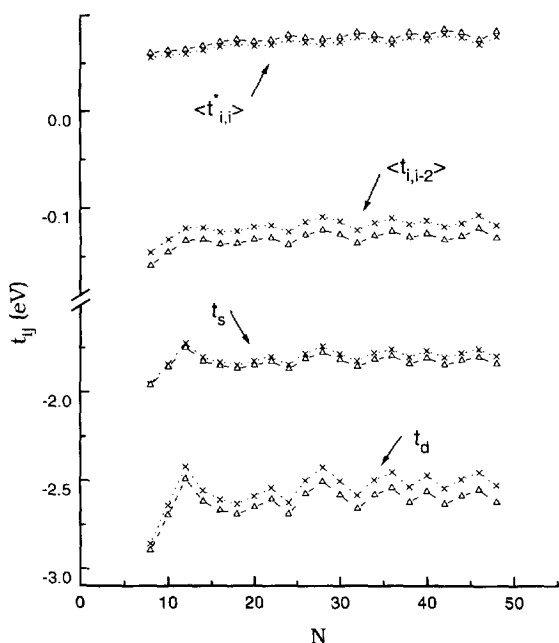


Fig. 1. t matrix elements versus N . Triangles (Δ) and crosses (\times) are for $a_0 = 1.0$ and 1.29 Å, respectively. t_d and t_s are the average transfer integrals for double and single bonds, respectively. $\langle t_{ii}^* \rangle$ and $\langle t_{i,i-2} \rangle$ are the average values of t_{ii}^* and $t_{i,i-2}$, respectively.

density matrix and compared with the original Hartree–Fock (GAUSSIAN) calculation used to construct the effective Hamiltonian. The comparison given in Table 2 shows that the two density matrices are very similar with a standard deviation of 2.7×10^{-5} .

t_{ii} varies with i primarily because the nuclear charge on each site is not zero which results in different Coulomb interactions between π electrons

and nuclei. Subtracting the Coulomb interaction arising from nuclei, we define,

$$t_{ii}^* = t_{ii} + \sum_j (V_{ij} - V_{1j}).$$

t_{ii}^* listed in Table 1 are very similar at all sites.

Using the same procedure, and keeping $U = 6.64$ eV, we determined effective Hamiltonians for even N between 8 and 48. In Fig. 1 we display t_d and t_s versus N . They are approximately -2.5 and -1.8 eV, respectively, and converge at $N \approx 14$. The resulting t_{ij} is transferable among different systems, reflecting the fact that the chemical bonding structures are similar when the polyenes are sufficiently large. This suggests the applicability of the effective Hamiltonian to larger systems.

Using these effective Hamiltonians, we have calculated the optical gaps for $N = 8, 10, 12, 14, 16,$ and 20 . The theoretical and experimental gaps of tetradecaheptaene are identical by the choice of U . In Table 3 we compare the calculated gaps with experiment [16]. The difference ranges from 0.01 to 0.2 eV. Given that the calculated geometries were not fitted to experiment and a minimal basis was employed, the consistency between theory and experiment is satisfactory.

To examine the validity of our neglect of long range transfer integrals (beyond nearest neighbor), we repeated the solution of Eq. (3) by including also next nearest neighbor hopping terms $t_{i,i \pm 2}$. In this case we found it necessary to introduce the following constraint in our variational calculation

$$\mathcal{F} = W \sum_{i=1}^{N-1} (t_{ii}^* - t_{i+1,i+1}^*)^2, \quad (6)$$

where $W = 0.02$ is a weighting constant. This constraint reflects our observation that the on-site ener-

Table 3
Comparison of theoretical and experimental optical gaps (in eV)

	$N = 8$	$N = 10$	$N = 12$	$N = 14$	$N = 16$	$N = 20$
Δ_{theo}^a	4.07	3.57	3.19	3.18	3.12	2.98
Δ_{theo}^b	4.04	3.55	3.18	3.18	3.13	3.00
Δ_{exp}^c	4.08	3.71	3.41	3.18	3.02	2.77

^a Calculations using $a_0 = 1.0$ Å.

^b Using $a_0 = 1.29$ Å.

^c Experimental results taken from Ref. [16].

Table 4
 D_m and D_s for different sizes.

	$N = 2$	$N = 4$	$N = 6$	$N = 8$	$N = 16$	$N = 24$	$N = 48$
D_m	1	3	5	7	15	23	47
D_s	0	2	5	10	44	102	420

gies t_{ii}^* are very similar. Without this constraint, the right side of Eq. (3) could not be inverted. The resulting transfer integrals for tetradecaheptaene are listed in Table 1. We note that the next nearest neighbor elements are an order of magnitude smaller than the nearest neighbor ones, and are approximately independent on i . This is to be expected from physical arguments. The resulting $t_{i,i\pm 1}$ are unchanged to the third decimal point compared with the previous calculations with $t_{i,i\pm 2} = 0$, as indicated in Table 1. In Fig. 1, we show the average next nearest hopping terms $\langle t_{i,i-2} \rangle$ for $N = 8$ to 48. We conclude that it is sufficient to include only the on-site and the nearest neighbor hopping matrix elements in the effective Hamiltonians of polyacetylene oligomers.

The average hopping terms t_d , t_s and $\langle t_{i,i-2} \rangle$ for octatetraene are -2.90 , -1.96 and -0.15 eV, respectively. Pariser and Parr used a semi-empirical method and determined that $(t_d, t_s) = (-2.92, -1.68)$ eV for butadiene [5]. Gavin and Rice determined $(t_d, t_s) = (-2.68, -2.02)$ eV for hexatriene by fitting PPP-SCI calculation to their experiment [19]. These values depend on the value of optical gap. For octatetraene, Sondheimer et al. found a gap of 4.08 eV for measurement in a solvent (isooctane) [16], whereas Heimbrook et al. reported a gap of 4.41 eV in the gas phase [20]. Freed and co-workers used a multireference configuration ab initio effective valence shell Hamiltonian calculation, and determined the hopping matrix elements $(t_d, t_s, \langle t_{i,i-2} \rangle)$ of trans-butadiene and hexatriene are $(-3.34, -2.57, 0.24)$ and $(-3.22, -2.53, 0.27)$ eV, respectively [10]. Their basis set is a double- ζ plus polarization (ccPVDZ) augmented with two carbon p Rydberg primitives [10,21]. The difference may reflect the different basis sets and different levels of ab initio calculations. Many workers employed $U = 11.13$ eV in the PPP model calculations [19]. However, Fukutome argued that owing to σ electrons a dielectric

constant ϵ of 1.5 to 2.0 is required to reproduce experimental results for polyacetylene of medium to large size [15]. $\epsilon = 1.5$ leads to $U = 7.42$ eV in Ref. [11].

To test the sensitivity of our results to a_0 , we have repeated our calculations using $a_0 = 1.29$ Å [11]. The resulting $\langle t_{ii}^* \rangle$, t_s , t_d and $\langle t_{i,i-2} \rangle$ are shown in Fig. 1. Note that $\langle t_{ii}^* \rangle$, $\langle t_{i,i-2} \rangle$ and t_s are almost the same. t_d differs by 0.1 eV ($\approx 4\%$).

The systems studied here have inversion symmetry. The Hartree–Fock molecular orbitals can be classified into A_g (symmetric) and B_u (anti-symmetric) types. Thus, the number of independent parameters needed to specify the Hartree–Fock ground state, D_s , is less than D_ρ . For $N = 2$, there are one A_g and one B_u orbitals which are uniquely determined by symmetry, and $D_s = 0$. For $N = 4$, there are two A_g and two B_u states; the Hartree–Fock ground state is made of four electrons occupying one A_g and one B_u ; and therefore, $D_s = 2$ using a previous argument for determining D_ρ . In Table 4 we list D_s for several sizes. These numbers represent the upper limits of the number of independent linear equations that Eq. (3) contains for centrosymmetric systems. Since for $N = 2$ and 4, $D_s < D_m$, there are no unique solutions of Eq. (4). $N = 6$ is a borderline case with $D_s = D_m$ and we found no unique solution in this case either. For $N \geq 8$, $D_s > D_m$; thus, it is possible to solve Eq. (4). We obtained a unique solution for every $N \geq 8$.

In conclusion, we demonstrated how the ground state reduced single-electron density matrix can be used to obtain the effective Hamiltonian, and that suitable constraints are needed to yield a unique solution. This work provides a direct link between ab initio calculations and theoretical formalisms based on effective Hamiltonians. The present method requires the information on ground state charge and bond orders distribution, solves a set of linear equations, and is computationally feasible for very large systems.

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