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Abstract. Based on an improved semi-empirical effective Hamiltonian method, computed electronic structures of clusters and linear chain crystals are reported. The ionization energies of clusters as a function of cluster size are examined to find correlation with bulk values as the cluster size further increases. The improved method is shown to remedy some failures of conventional semi-empirical methods. Some of the salient features from the present study are the improvement of the first ionization energies, the satisfactory prediction of work function, a newly found linear relationship between the ionization energies and the inverse of cluster size, $1/n$, for the molecular clusters of $(H_2O)_n$. In addition, predicted band structures for one-dimensional organic crystals and ice are discussed.

1. Introduction

For self-consistent field HF (Hartree–Fock) LCAO (linear combination of atomic orbitals) calculations for crystals, various levels of direct [1–16] and reciprocal [17, 18] lattice vector space approaches have been employed. Others include the $X\alpha$ scattering wave [19], *ab initio* extended muffin-tin orbital [20], and localized orbital methods [21] to name a few. In order to avoid excessive computational time, semi-empirical valence-electron methods [8–16, 21–25] are often employed. Among the semi-empirical methods, MNDDO [25] (modified NDDO [23]—(neglect of diatomic differential overlap) is one of the most recently developed methods, and has rapidly become one of the most widely used methods. Recently, its application to clusters, crystals, and surfaces has greatly increased [15, 16, 26–34].

In this study, we present both the formal description of a semi-empirical effective Hamiltonian treatment and its application to clusters and crystals. The clusters referred to here are the aggregated states of either atoms or molecules. The physical properties of the clusters are then expected to be intermediate between the atomic (or molecular) and bulk properties. When the number of atomic or molecular units in the clusters is sufficiently large, some physical properties of the clusters are expected to converge to the bulk limits of crystals. Thus it will be of great interest to examine the variation of

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physical properties as a function of cluster size in order to see how they converge to some of the bulk properties. Our improved method of treating molecular clusters and crystals will be shown to remedy the failure of semi-empirical theories in accounting for inter-molecular binding. Variation of the first ionization energy as a function of cluster size will be examined in order to see the trend of its convergence to the bulk limit of linear crystals. Geometry optimization is often ignored in the study of clusters and crystals. In the present study, we would like to stress that the reported results for both the clusters and crystals are based on geometry optimization.

2. Electronic structure study of molecular clusters and infinite linear chain (1D) crystals

Parameters in the conventional semi-empirical methods [1] are selected by fitting physical properties for isolated molecules (monomers), based on geometries wherein their equilibrium interatomic distances are much shorter compared to intermolecular sep-arations between molecular units in molecular clusters or molecular crystals. For this reason semi-empirical methods are likely to fail in reproducing observed properties, particularly for the molecular clusters or crystals whose formation is primarily due to intermolecular interaction. Indeed, earlier we found that the conventional semi-empirical methods are reliable only for the isolated molecules, not for the molecular clusters [35], thus requiring a correct account of the long-range intermolecular inter-action. For this reason, in our semi-empirical effective Hamiltonian treatment we divide parameters into two sets: one for the intramolecular interaction and the other for the intermolecular interaction in accordance with the expressions (46) to (48) (see later).

   In addition to the separation of the intramolecular and intermolecular interactions in treating the semi-empirical effective Hamiltonian, we introduce the core–core repulsion energy which is differently treated from the original MNDDO [25] due to the successful two-parameter set effective Hamiltonian approach that we proposed elsewhere [29, 35]. It is written, in accordance with our earlier work [29, 35]

$$E_{ab} = Z_a Z_b (s_a s_a | s_b s_b)[1 + \gamma_{ab} \exp(-\alpha_{ab} r_{ab}]$$

for the pairs of atoms a and b. Here r_{ab} is the interatomic distance between a and b; γ and α are the parameters to be chosen by fitting measurements; Z_a and Z_b are the core charges of atoms a and b respectively. $(s_a s_a | s_b s_b)$ above is the two-electron two-centre integrals involving the s atomic orbitals in the two different atoms a and b. In our calculations these two-centre integrals are taken from the original MNDDO parameter values. In parallel with our earlier study of molecular clusters, in the following we introduce an effective Hamiltonian method for molecular clusters.

   The valence-electron Hamiltonian for molecular crystals is, in atomic units,

$$H = \sum_p^{(2N+1)^3} \sum_\alpha^{n_e} h_\alpha(\boldsymbol{p}) + \sum_{p,q}^{(2N+1)^3} \sum_{\alpha<\beta}^{n_e} V_{\alpha\beta}(\boldsymbol{p}, \boldsymbol{q}). \tag{1}$$

Here the first term is the one-electron energy operator made up of the kinetic energy and nuclear attraction energy terms respectively:

$$h_\alpha(\boldsymbol{p}) = -\tfrac{1}{2}\nabla_\alpha^2 - \sum_q^{(2N+1)^3} \sum_a^{n_a} Z_a |r_\alpha^p - R_a^q|^{-1} \tag{2}$$

and the second term is the two-electron repulsion energy operator:

$$V_{\alpha\beta}(\boldsymbol{p}, \boldsymbol{q}) = |r_\alpha^p - r_\beta^q|^{-1}. \tag{3}$$

The symbol definitions in (1) to (3) are as follows: $\boldsymbol{p}$ and $\boldsymbol{q}$ are the vector indices (integers)

to locate unit cells with each component of p and q running over integers $-N$, $-(N-1)$, $\ldots, 0, \ldots, (N-1)$, N; α and β, the electron indices; n_e, the total number of valence electrons in the unit cell; r_α^p, the position vector of electron α in the unit cell p; Z_a, the core charge (nuclear charge—inner shell electron charge) number; R_a^q, the position vector of atom a in the unit cell q; and n_a, the number of atoms in the unit cell. $\alpha < \beta$ in (1) represents a single counting of interaction between any two electrons.

Introducing the average (Hartree–Fock) potential, U_α^o, Hamiltonian (1) is cast into

$$H = H^o + H' \tag{4}$$

where H^o is the Hartree–Fock one-electron Hamiltonian:

$$H^o = \sum_p \sum_\alpha \left(h_\alpha(p) + U_\alpha^o(p) \right) \tag{5}$$

and H', the residual interaction:

$$H' = \sum_{p,q} \sum_{\alpha < \beta} V_{\alpha\beta}(p,q) - \sum_p \sum_\alpha U_\alpha^o(p). \tag{6}$$

We now rewrite (6) in the form of pair-wise residual interaction $U_{\alpha\beta}$:

$$H' = \sum_{p,q} \sum_{\alpha < \beta} U_{\alpha\beta}(p,q) \tag{7}$$

where

$$U_{\alpha\beta}(p,q) = V_{\alpha\beta}(p,q) - (U_\alpha^o(p) + U_\beta^o(q))/(M-1) \tag{8}$$

with

$$M = n_e(2N+1)^3. \tag{9}$$

We can rewrite (5) and (6) in the form of second quantization:

$$H^o = \sum_{p,q} \langle i^p | h_\alpha + U_\alpha^o | j^q \rangle \, a_i(p)a_j(q) \tag{10}$$

and

$$H' = \tfrac{1}{2} \sum_{p,q,r,s} \sum_{i,j,k,l} \langle i^p j^q | V_{\alpha\beta} | k^r l^s \rangle a_i(p)^+ a_j(q)^+ a_l(s)a_k(r)$$

$$- \sum_{p,q} \sum_{ij} \langle i^p | U_\alpha^o | j^q \rangle a_i(p)^+ a_j(q) \tag{11}$$

where i, j, k, and l are the spin orbital indices and $|i^p\rangle$, the crystal orbital belonging to the pth irreducible representation.

The crystal orbitals i are written, in terms of the LCAO expansion,

$$\Psi_i^p(r) = \sum_\mu^n C_{\mu i}(p)\varphi_\mu^p(r). \tag{12}$$

Here μ runs over all the atomic orbitals in the unit cell. $C_{\mu i}$ is the expansion coefficient

which 'weighs' the contribution of the atomic orbital μ to the ith crystal orbital. The atomic Bloch functions are written by

$$\varphi_\mu^p(r) = \sum_q \exp[ip \cdot q/(2N+1)^3]\varphi_\mu(r - R^q) \tag{13}$$

where R^q is the position vector of an atom belonging to the unit cell q and φ_μ, the μth atomic orbital.

A set of infinite orthonormal electronic configuration states (determinants) can be constructed from the crystal orbitals defined above. Using the orthonormal set, we define the projection operator [36]

$$P = |0\rangle\langle 0| \tag{14}$$

which projects onto the vacuum state $|0\rangle$, i.e. the Hartree–Fock ground state, and

$$q = |k\rangle\langle k| \tag{15}$$

which projects onto the excited configuration states (determinants) $|k\rangle$. They satisfy

$$P + Q = 1 \tag{16}$$

and

$$PQ = QP = 0. \tag{17}$$

Using the relations (14) to (17) for the Schrödinger equation

$$H\Psi = E\Psi \tag{18}$$

we obtain the coupled Schrödinger equations of

$$PH(P + Q)\Psi = EP\Psi \tag{19}$$

and

$$QH(P + Q)\Psi = EQ\Psi. \tag{20}$$

The substitution of (20) into (19) leads to

$$\bar{H}_{pp}|0\rangle = E|0\rangle \tag{21}$$

where

$$\bar{H}_{pp} = P(H + HQ(E - QHQ)^{-1}QH)P. \tag{22}$$

Realizing that $PHQ = PH'Q$ and $QHP = QH'P$, the expression (22) above is reduced to

$$\bar{H}_{pp} = P\bar{H}P \tag{23}$$

where

$$\bar{H} = H + \bar{H}' \tag{24}$$

with

$$\bar{H}' = H'Q(E - QHQ)^{-1}QH' \tag{25}$$

or

$$\bar{H}' = H'Q(E - QH^\circ Q)^{-1}QH'$$

$$+ H'Q(E - QH^oQ)^{-1}H'(E - QH^oQ)^{-1}QH' + \ldots. \tag{26}$$

The true total electronic energy is then simply

$$E = \langle 0|\bar{H}|0\rangle = E^o + E' \tag{27}$$

where

$$E^o = \langle 0|H|0\rangle \tag{28}$$

is the familiar Hartree–Fock energy, and

$$E' = \langle 0|\bar{H}'|0\rangle \tag{29}$$

is the correlation energy, which is formally written, by using (10), (11), and (26):

$$
\begin{aligned}
E' = \sum_{p,q,r,s} \sum_{i,j,k,l} & \langle i^p j^q | V_{\alpha\beta} | k^r l^s \rangle \langle k^r l^s | V_{\alpha\beta} | i^p j^q \rangle \\
& \times \langle 0|a_i(\boldsymbol{p})^+ a_j(\boldsymbol{q})^+ a_l(\boldsymbol{s}) a_k(\boldsymbol{r})(E - QH^oQ)^{-1} a_k(\boldsymbol{r})^+ a_l(\boldsymbol{s})^+ a_j(\boldsymbol{q}) a_i(\boldsymbol{p})|0\rangle \\
& + \langle i^p j^q | V_{\alpha\beta} | k^r l^s \rangle \langle k^r l^s | V_{\alpha\beta} | i^p j^q \rangle \\
& \times \langle 0|a_i(\boldsymbol{p})^+ a_j(\boldsymbol{q})^+ a_k(\boldsymbol{r}) a_l(\boldsymbol{s})(E - QH^oQ)^{-1} a_k(\boldsymbol{r})^+ a_l(\boldsymbol{s})^+ a_j(\boldsymbol{q}) a_i(\boldsymbol{p})|0\rangle \\
& - \sum_{p,r} \sum_{i,k} \langle i^p | U_\alpha^o | k^r \rangle \langle k^r | U_\alpha^o | i^p \rangle \\
& \times \langle 0|a_i(\boldsymbol{p})^+ a_k(\boldsymbol{r})(E - QH^oQ)^{-1} a_k(\boldsymbol{r})^+ a_i(\boldsymbol{p})|0\rangle + \ldots. \tag{30}
\end{aligned}
$$

In the expression above the crossed term between the direct and exchange interaction and higher order terms are omitted.

Obviously direct evaluation of the correlation energy (30) above is not readily feasible and will be circumvented here. The introduction of (7) into (26) yields

$$\bar{H}' = \sum_{p,q} \sum_{\alpha < \beta} W_{\alpha\beta}(\boldsymbol{p}, \boldsymbol{q}) \tag{31}$$

where

$$
\begin{aligned}
W_{\alpha\beta}(\boldsymbol{p}, \boldsymbol{q}) = U_{\alpha_p\beta_q}(E - QH^oQ)^{-1} \\
\times \left(\sum_{r,s} \sum_{\gamma_r < \delta_s} U_{\gamma_r\delta_s} + \sum_{t,u} \sum_{\lambda_t < \mu_u} U_{\lambda_t\mu_u}(E - QH^oQ)^{-1} \sum_{v,w} \sum_{\gamma_v < \delta_w} U_{\gamma_v\delta_w} + \ldots \right). \tag{32}
\end{aligned}
$$

Later two-electron integrals associated with $W_{\alpha\beta}$ will be subject to a semi-empirical treatment.

Using (1) and (31) above, we now rewrite (24):

$$\bar{H} = \sum_p \sum_\alpha h_\alpha(\boldsymbol{p}) + \sum_{p,q} \sum_{\alpha < \beta} [V_{\alpha\beta}(\boldsymbol{p}, \boldsymbol{q}) + W_{\alpha\beta}(\boldsymbol{p}, \boldsymbol{q})]. \tag{33}$$

Applying the usual procedure of the variational method to the total electronic energy (27),

$$E = \langle 0| \sum_p \sum_\alpha h_\alpha(\boldsymbol{p}) + \sum_{p,q} \sum_{\alpha < \beta} [V_{\alpha\beta}(\boldsymbol{p}, \boldsymbol{q}) + W_{\alpha\beta}(\boldsymbol{p}, \boldsymbol{q})]|0\rangle \tag{34}$$

we obtain the one-electron Schrödinger equation of the form

$$\mathcal{H}(\boldsymbol{p})|i^p\rangle = \varepsilon_i(\boldsymbol{p})|i^p\rangle. \tag{35}$$

Here $\mathcal{H}(\boldsymbol{p})$ represents the effective one-electron Hamiltonian:

$$\mathcal{H}(\boldsymbol{p}) = h(\boldsymbol{p}) + \sum_i^m [2J_i(\boldsymbol{p}) - K_i(\boldsymbol{p})] \tag{36}$$

where

$$J_i(p) = \int \Psi_i^p(r_\beta)^* (V_{\alpha\beta} + W_{\alpha\beta}) \Psi_i^p(r_\beta) \, dr_\beta \tag{37}$$

with

$$K_i(p)\Psi_j^p(r_\alpha) = \int [\Psi_i^p(r_\beta)^*(V_{\alpha\beta} + W_{\alpha\beta})\Psi_j^p(r_\beta) \, dr_\beta] \, \Psi_i^p(r_\alpha) \tag{38}$$

and

$$\langle r_\beta | i^p \rangle = \Psi_i^p(r_\beta). \tag{39}$$

For simplicity the electron index α is dropped in (36) above. It is now easily seen that if electron correlation is ignored (that is, $W_{\alpha\beta} = 0$), the effective one-electron Hamiltonian (36) above is reduced to the familiar form of the Hartree–Fock Hamiltonian.

To treat infinite linear chain molecular crystals, the block diagonalized matrix of the effective one-electron Hamiltonian becomes

$$\mathcal{H}_{\mu\nu}(k) = \sum_{q=0}^{\infty} [\exp(ikqa)\mathcal{H}_{\mu^o\nu^q} + \exp(-ikqa)\mathcal{H}_{\nu^o\mu^q}](1 - \tfrac{1}{2}\delta_{oq}). \tag{40}$$

Here $\mathcal{H}_{\mu^o\nu^q}$ are the matrix elements of $\mathcal{H}(q)$ between the atomic orbitals, μ^o belonging to the reference unit cell o and ν^q belonging to the unit cell q and are explicitly

$$\mathcal{H}_{\mu^o\nu^q} = \int \varphi_{\mu^o}(r_\alpha)h(r_\alpha)\varphi_{\nu^q}(r_\alpha) \, dr_\alpha$$

$$+ \sum_{s,t}\sum_{\lambda\sigma} D_{\lambda^s\sigma^t} \left(\int \varphi_{\mu^o}^*(r_\alpha)\varphi_{\lambda^s}^*(r_\beta)(V_{\alpha\beta} + W_{\alpha\beta}) \right.$$

$$\times \varphi_{\nu^q}(r_\alpha)\varphi_{\sigma^t}(r_\beta) \, dr_\alpha \, dr_\beta - \tfrac{1}{2}\int \varphi_{\mu^o}^*(r_\beta)\varphi_{\lambda^s}^*(r_\beta)(V_{\alpha\beta} + W_{\alpha\beta})$$

$$\left. \times \varphi_{\sigma^t}(r_\alpha)\varphi_{\nu^q}(r_\beta) \, dr_\alpha \, dr_\beta \right) \tag{41}$$

with

$$D_{\lambda^s\sigma^t} = \sum_j \frac{a}{\pi} \int_{-\pi/a}^{\pi/a} C_{\lambda^sj}^*(k)C_{\sigma^tj}(k) \, e^{i(t-s)ka} \, dk \tag{42}$$

where $D_{\lambda^s\sigma^t}$ is the charge density matrix element for one-dimensional crystals. μ, ν, λ, and σ in (41) are the atomic orbital indices. q, s, and t are the cell indices. a is the primitive translation for the linear chain crystals.

Now writing

$$\langle \mu^o | h | \nu^q \rangle = \int \varphi_{\mu^o}^*(r_\alpha)h(r_\alpha)\varphi_{\nu^q}(r_\alpha) \, dr_\alpha \tag{43}$$

and

$$\Gamma_{\mu^o\lambda^s}^{\nu^q\sigma^t} = \int \varphi_{\mu^o}^*(r_\alpha)\varphi_{\lambda^s}^*(r_\beta)(V_{\alpha\beta} + W_{\alpha\beta})\varphi_{\nu^q}(r_\alpha)\varphi_{\sigma^t}(r_\beta) \, dr_\alpha \, dr_\beta \tag{44}$$

the expression (41) is simply

$$\mathcal{H}_{\mu^o\nu^q} = \langle \mu^o | h | \nu^q \rangle + \sum_{s,t}\sum_{\lambda\sigma} D_{\lambda^s\sigma^t} [\Gamma_{\mu^o\lambda^s}^{\nu^q\sigma^t} - \tfrac{1}{2}\Gamma_{\mu^o\lambda^s}^{\sigma^t\nu^q}]. \tag{45}$$

Here the first term is the familiar one-electron integral and the second term includes

correlation through the two-electron integrals Γ due to the residual interaction $W_{\alpha\beta}$. The two-electron integrals Γ are determined by parametrization.

The expression (45) above represents the matrix elements of a generalized effective (semi-empirical) Hamiltonian $\mathcal{H}$. Here the effects of correlation are now seen to be introduced only through the two-electron integrals Γ. We choose the NDDO (neglect of diatomic differential overlap) approximation [23] for the evaluation of the two-electron multi-centre integrals Γ. Further we divide the matrix elements $\mathcal{H}_{\mu_a^o\nu_b^o}$ into two sets, intramolecular and intermolecular matrix elements. Thus we obtain, for the intramolecular matrix elements,

$$\mathcal{H}_{\mu_a^o\nu_a^o} = \langle\mu_a^o|h|\nu_a^o\rangle + \sum_{\lambda_a^o\sigma_a^o} D_{\lambda_a^o\sigma_a^o} \left(\Gamma_{\mu_a^o\lambda_a^o}^{\nu_a^o\sigma_a^o} - \tfrac{1}{2}\Gamma_{\mu_a^o\lambda_a^o}^{\sigma_a^o\nu_a^o}\right) \tag{46}$$

which represents the matrix element between the atomic orbitals μ_a^o and ν_a^o both belonging to the same atom a in the same cell o, and

$$\mathcal{H}_{\mu_a^o\nu_b^o} = \langle\mu_a^o|h|\nu_b^o\rangle - \tfrac{1}{2}\sum_{\lambda_b^o\sigma_a^o} D_{\lambda_b^o\sigma_a^o}\Gamma_{\mu_a^o\lambda_b^o}^{\sigma_a^o\nu_b^o} \tag{47}$$

which represents the matrix element between an atomic orbital μ_a^o belonging to an atom a and an orbital ν_b^o belong to a different atom b in the same cell o. Now for the intermolecular matrix elements we obtain

$$\mathcal{H}_{\mu_a^o\nu_b^q} = \langle\mu_a^o|h|\nu_b^q\rangle - \tfrac{1}{2}\sum_{\lambda_b^q\sigma_a^o} D_{\lambda_b^q\sigma_a^o}\Gamma_{\mu_a^o\lambda_b^q}^{\sigma_a^o\nu_b^q} \tag{48}$$

representing the matrix elements between an atomic orbital μ_a^o belonging to an atom a in the cell o and an orbital ν_b^q belonging to a different atom b in cell q.

For the sake of connection with the kth block diagonalized matrix for the effective one-electron Hamiltonian for one-dimensional crystals, we now write [1]

$$\mathcal{H}(k) = \sum_{q=-\infty}^{\infty} \exp(ik \cdot R_q)\mathcal{H}(q) \tag{49}$$

with the matrix size of $n \times n$, where n is the total number of atomic orbitals available in the unit cell. Here the matrix element of $\mathcal{H}(q)$ is given by

$$\mathcal{H}_{\mu^o\nu^q} = \langle\mu^o|\mathcal{H}|\nu^q\rangle \tag{50}$$

with μ^o indicating the atomic orbital μ belonging to the reference unit cell o and ν^q, the atomic orbital ν in the unit cell q. k is the wavevector whose ith component is given by

$$k_i = 2\pi p_i/[a_i(2N+1)] \tag{51}$$

with the range of $-\pi/a_i < k_i < \pi/a_i$ and the direct lattice vector,

$$R_q = q_1\hat{a}_1 + q_2\hat{a}_2 + q_3\hat{a}_3 \tag{52}$$

where $\hat{a}_i$ are the basis vectors of the crystal.

The matrix elements (1) are explicitly

$$\mathcal{H}_{\mu^o\nu^q} = \int \varphi_{\mu^o}^*(r_\alpha)h(r_\alpha)\varphi_{\nu^q}(r_\alpha)\,dr_\alpha$$

$$+ \sum_{s,t}\sum_{\lambda\sigma} D_{\lambda^s\sigma^t}\left(\int \varphi_{\mu^o}^*(r_\alpha)\varphi_{\lambda^s}^*(r_\beta)(V_{\alpha\beta} + W_{\alpha\beta})\varphi_{\nu^q}(r_\alpha)\varphi_{\sigma^t}(r_\beta)\,dr_\alpha\,dr_\beta\right.$$

$$- \tfrac{1}{2} \int \varphi_{\mu^o}^*(\boldsymbol{r}_\beta) \varphi_{\lambda^s}^*(\boldsymbol{r}_\beta)(V_{\alpha\beta} + W_{\alpha\beta}) \varphi_{\sigma^t}(\boldsymbol{r}_\alpha) \varphi_{\nu q}(\boldsymbol{r}_\beta)\, \mathrm{d}\boldsymbol{r}_\alpha\, \mathrm{d}\boldsymbol{r}_\beta \Big) \tag{53}$$

where D is the charge density matrix:

$$D_{\lambda^s\sigma^t} = \frac{2}{\Omega} \sum_j^m \int_\Omega C_{\lambda^s j}^*(\boldsymbol{k}) C_{\sigma^t j}(\boldsymbol{k}) \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_t - \boldsymbol{R}_s)]\,\mathrm{d}\boldsymbol{k}. \tag{54}$$

Here Ω is the volume of the first Brillouin zone and $C(\boldsymbol{k})$, the expansion coefficient vector. The crystal orbital energy or the energy band $\varepsilon(\boldsymbol{k})$ is obtained from [1]

$$\mathcal{H}(\boldsymbol{k})C(\boldsymbol{k}) = \varepsilon(\boldsymbol{k})S(\boldsymbol{k})C(\boldsymbol{k}). \tag{55}$$

$S(\boldsymbol{k})$ is the kth block of the block diagonalized matrix for the overlap integral.

Now the consideration of translational symmetry in (53) leads, for one-dimensional crystals, to

$$\mathcal{H}_{\mu^o\nu^{-q}} = \mathcal{H}_{\mu^o\nu q}. \tag{56}$$

The matrix $\mathcal{H}(\boldsymbol{k})$ in (49) satisfies the hermiticity

$$\mathcal{H}(\boldsymbol{k})^+ = \mathcal{H}(\boldsymbol{k}). \tag{57}$$

Thus the matrix element of the effective one-electron Hamiltonian (49) can be rewritten:

$$\mathcal{H}_{\mu\nu}(\boldsymbol{k}) = \sum_{q=0}^{\infty} (\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_q}\mathcal{H}_{\mu^o\nu q} + \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_q}\mathcal{H}_{\mu^o\nu q})(1 - \tfrac{1}{2}\delta_{oq}). \tag{58}$$

For comparison, we present two different treatments for the semi-empirical effective Hamiltonian matrix. One is the separation of the matrix into the intramolecular and intermolecular interactions as shown in (46) through (48) and the other treatment is no separation between the two. The latter is thus a single intramolecular parameter set approach equivalent to the conventional semi-empirical method known as MNDDO [25]. We consider the latter first, for studying both the finite and infinite 'clusters' of $H(CH_2)_nH$ and $(CH_2)_\infty$ respectively. They are namely the n-alkane molecules and the infinite linear chain polyethylene crystal. Here n is the number of CH_2 units in n alkanes. In our present work all of the calculated results for the organic crystals and polyatomic cluster systems of interest are based on geometry optimization.

It is of note that among the computed n-alkanes listed in table 1, only the two molecules of CH_4 and C_2H_6 were used in the original parameterization [25]. Thus it is of great interest to see how well both the first ionization energies of the remaining large organic 'clusters', i.e. n-alkanes, $H(CH_2)_nH$ with $n > 2$ and the electronic structure of the infinite linear chain organic crystal of polyethylene agree with observations. The predicted ionization energies for all the n-alkane molecules and polyethylene are consistently in better agreement with the observed values [37] compared to *ab initio* HF [6], as shown in figure 1(*a*). The *ab initio* HF (in which electron correlation is absent) predicted the increasing divergence of ionization energy from observation as the cluster size n increases. This suggests that the role of electron correlation becomes increasingly important as n increases. The measurements of photoelectron spectra [37] show a systematic decrease in the values of ionization potentials with the increase of size n and the propensity of a linear relationship between the ionization energy and the inverse of molecular or cluster size, $1/n$. Encouragingly, such a linear relationship is correctly predicted with the one-parameter set semi-empirical effective Hamiltonian MNDDO

Table 1. First ionization energies (eV) of *n*-alkanes and polyethylene.

Molecule	PES [36] (eV)	*Ab initio* [6] (eV)	MNDDO [15] (eV)
CH_4	14.0	16.3	13.9
C_2H_6	12.1	14.7	12.7
n–C_3H_8	11.5	14.3	12.3
n–C_4H_{10}	10.67	13.9	12.2
n–C_5H_{12}	10.37	—	12.2
n–C_6H_{14}	10.18	—	12.0
n–C_7H_{16}	9.90	—	12.0
n–C_8H_{18}	—	—	11.9
n–C_9H_{20}	—	—	11.9
n–$C_{10}H_{22}$	—	—	11.8
$(CH_2)_x$	9.0	13.2	11.4
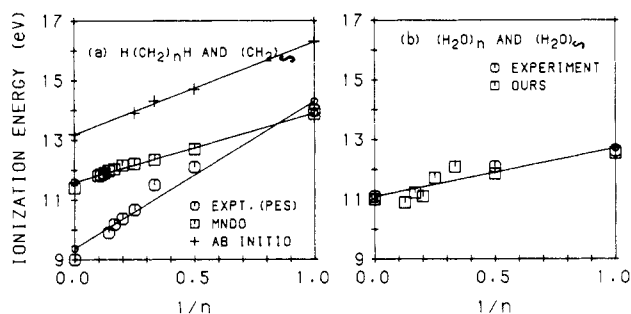
Figure 1. (*a*) The first ionization energy against $1/n$ for $H(CH_2)_nH$ and $(CH_2)_x$ or $(C_2H_4)_x$. (*b*) The first ionization energy against $1/n$ for $(H_2O)_n$ and $(H_2O)_x$; the open circles denote predicted values, the open squares observed values, and the crosses represent *ab initio* calculations.

method [25] which is employed here. As in the *ab initio* calculation this method also showed an increasing deviation of ionization energy from observation as size *n* increases.

Although not sufficient, small correlation effects are introduced in the semi-empirical treatment above, judging from comparison between its predicted band gap of 6.5 eV and *ab initio* HF value of 7.3 eV [7] for alternant-bond trans-polyacetylene $(C_2H_2)_x$ (or simply $(CH)_x$). Its predicted valence band structure is shown in figure 2(*a*). We find that the difference between the observed [38, 39] and predicted ionization energies for the linear chain crystal of alternant-bond trans-polyacetylene is 2.9 eV. In general the effects of correlation raise the occupied valence band and lower the conduction band [40]. Only for a qualitative estimation of correlation correction for band gaps, the occupied π valence band energy for polyacetylene is raised by 2.9 eV, and the π^* conduction band energy lowered by the same amount. Subtracting the combined correlation energy correction of 5.8 eV from the predicted band gap of 6.5 eV, we obtain the band gap of 0.7 eV. Interestingly, this value becomes reasonably close to the predicted band gap of 0.8 eV from the first principles LCAO, extended tight binding EH calculation of Grant and Batra [9] and the observed band gap of 1.4 eV [38]. Encouragingly, similar correction made for polyethylene leads to the band gap of 9.7 eV, again yielding better agreement
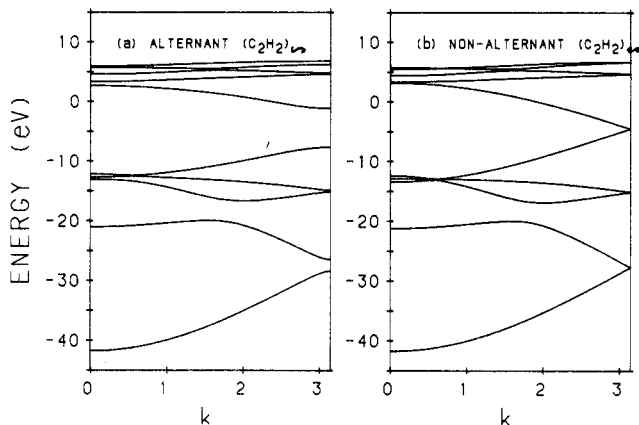
Figure 2. (*a*) Valence band structure of alternant-trans-polyacetylene $(CH)_x$ or $(C_2H_2)_x$. (*b*) Valence band structure of non-alternant-trans-polyacetylene $(CH)_x$ or $(C_2H_2)_x$.

with the observed band gap of 7.5 ± 0.5 eV [6] compared with the uncorrected band gap of 14.5 eV [15]. Thus it is possible to introduce such correlation correction for improved estimations of band gaps by using only the experimental values of the first ionization energies of large clusters and the predicted band gaps of crystals. For the sake of completeness, in figure 2(*b*) we report the valence band structure of regular (non-alternant-bond) trans-polyacetylene, which belongs to screw rotation symmetry [11]. The predicted band gap is 0 eV in agreement with the symmetry condition and its band structure is predicted to be similar to that of the alternant-bond trans-polyacetylene crystal shown in figure 2(*a*). Geometry optimization yielded the equilibrium C–C bond length of 1.39 Å for the non-alternant-bond trans-polyacetylene. For the alternant-bond crystal, the double bond (C=C) length of 1.34 Å and the single bond (C–C) length of 1.44 Å were predicted. Encouragingly this is in excellent agreement with measurements [38, 39]. We find the lower end (near $k = 0$) of the π band to be of σ-type, in agreement with the CNDO/S2 calculation of Duke and co-workers and with the measurement of ultraviolet photoemission spectra [4]. The π^* conduction band state is found to be bound in agreement with the extended tight-binding EH study of Grant and Batra [9]. However, both the semi-empirical and *ab initio* methods predict larger band gaps than observed. This failure comes from the insufficiency of introducing correlation correction in the conventional one-parameter set semi-empirical effective Hamiltonian treatment and the entire neglect of correlation in the *ab initio* HF.

   As pointed out above, the predicted ionization energies for the organic 'clusters' of n-alkanes were seen to diverge as size n increases, indicating insufficient accounting of correlation effects by the effective Hamiltonian treatment, which introduces only a single parameter set. For this reason it will be of great interest to examine how a generalized semi-empirical effective Hamiltonian treatment discussed in section 2 corrects such failure. Now we examine the molecular clusters of $(H_2O)_n$ and infinite linear chain 'ice' $(H_2O)_x$, by using the generalized effective Hamiltonian. Previously it was shown that the one-parameter set effective Hamiltonian treatment described above completely failed even for the hydrogen-bonded molecular clusters of $(H_2O)_n$ in both binding energy and geometric structure [29, 35]. We avoid descriptions of molecular cluster calculations and of parameterization procedure as they appear elsewhere [29,
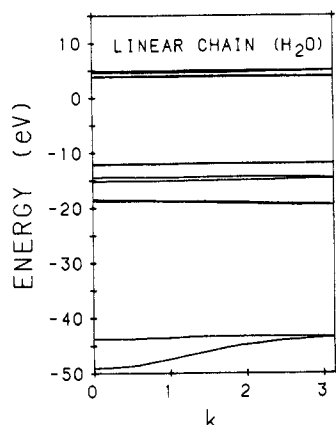
Figure 3. Valence band structure of infinite linear chain $(H_2O)_x$.

35]. In our calculations the geometric structures of clusters $(H_2O)_n$ are taken from various portions of the hexagonal ice I [43]. As shown in figure 1(b), the first ionization energy decreases with cluster size n. Interestingly we find that there exists the propensity of near linearity between predicted ionization energy and the inverse of cluster size, $1/n$. Convergence close to the observed work function (~ 11.0 eV) [44] of bulk ice is well predicted. It should be pointed out that the convergence from a finite to a bulk value can be extremely slow for certain physical properties [45]. This is a significant improvement over the one-parameter set semi-empirical treatment made for studying the molecular clusters and crystals. In figure 3 we show the band structure of infinite linear chain ice, $(H_2O)_x$ with the unit cell made of dimers $(H_2O)_2$. The predicted band gap is ~ 16 eV and the optimized geometry of O—H---O bond length, 2.86 Å. Predicted valence band widths are found to be narrow for both occupied and unoccupied bands as expected for the hydrogen-bonded 1D ice crystal. It will be of great interest to see how well the band gap of one-dimensional ice correlates with the future calculation of three-dimensional ice crystals, using the present level of approximate effective Hamiltonian method.

It should be noted that there are other proposed effective Hamiltonian techniques [46–48] currently available for the systems of current interest and that the difficulty of long-range interactions has been fully described and actual efforts for improvement have been made by some researchers in this field [49–53].

3. Summary

In this study we examined both the finite systems of clusters and infinite systems of one-dimensional organic crystals and ice by introducing the conventional semi-empirical method and a generalized semi-empirical effective Hamiltonian treatment. Using the conventional semi-empirical method [25] which employs only a single intramolecular parameter set, we found divergence in ionization energy for n-alkanes from observation as cluster size n increased, and the failure of band gaps for infinite linear chain organic crystals. On the other hand, the generalized effective Hamiltonian method was shown to correct such failure for the molecular clusters of $(H_2O)_n$. In view of the failure of accurate ionization energies and band gaps for the organic systems with the conventional semi-empirical methods, work will be resumed on further improvement by introducing

a new semi-empirical Hamiltonian approach in the same spirit as the satisfactory two-parameter set semi-empirical method that we devised for the study of molecular clusters in the current work.

In short, some findings from the present studies are (1) the improvement of the first ionization energies for the molecular clusters of all sizes with the generalized semi-empirical effective Hamiltonian treatment, (2) the satisfactory prediction of a linearity between the first ionization energies and the inverse of cluster size, $1/n$, in agreement with observation, and (3) the feasibility of qualitative correlation correction for band gaps in comparison with observation. In this study we have found some salient features with the conventional semi-empirical treatment, namely the satisfactory predictions of equilibrium geometries for clusters and crystals and a linear relationship between the ionization energies of clusters and the inverse of cluster size, $1/n$. This is consistent with the work of Cao and co-workers [54].

Acknowledgment

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