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Non-Empirical Molecular Orbital Theory of the Electronic Structure of Molecular Crystals

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A non-empirical molecular orbital treatment of molecular crystals, based on SCF perturbation theory and matrix partitioning methods is presented.

Key words: Molecular crystals, electronic structure of ~

1. Introduction

Applications [1–4] of molecular orbital theory to the calculation of the electronic structure of infinite systems are conventionally based on the use of Bloch's theorem [5]. The crystal or polymer SCF (Self Consistent Field) matrix equation is partially factorized by using the translational symmetry of the lattice to construct symmetry adapted orbitals. These orbitals are characterized by wave-vectors, k, which label the irreducible representations of the translational subgroup. The application of this method to one-dimensional polymers and crystals is relatively straightforward since the wave-vector may be treated as a scalar quantity under these circumstances. However, in the case of a three-dimensional crystal, this approach is rather more complicated. Since k must now be treated as a vector, with three independent components, a large number of values must be sampled in reciprocal space in order to achieve an acceptably accurate representation of an infinite three-dimensional crystal. Another, more subtle, problem is brought out by the group theoretical result first derived by Bouchaert, Smoluchowski and Wigner [6]. The factorization of the Fock equations obtained by transforming to translational-symmetry adapted basis orbitals is substantially less effective in the case of three-dimensional crystals. In general, a wave-vector, k, characterizing an irreducible representation of the translational subgroup is related, by the unit cell symmetry elements, to a number of other wave-vectors. A set of wave-vectors related in this way is called a star [6]. When the equations for the crystal are block diagonalized by the transformation, the sizes of the diagonal blocks are determined by the numbers of symmetrized orbitals associated with stars rather than with individual wave-vectors. Finally, from a physical point of view, these symmetry adapted orbitals do not provide the most appropriate starting point for calculations on molecular crystals. The known molecular character of these systems suggests that the electrons in the lattice are strongly localized on the molecules that constitute the crystal. The symmetry adapted orbitals, on the other hand, describe the electronic structure in terms of completely delocalized electrons. Thus, while these orbitals are suitable for theoretical studies on metallic crystals, their use for studies on molecular crystals must lead to excessive and unnecessary computing.

Recently, an alternative approach to the theoretical study of three-dimensional molecular crystals was reported [7–12], which avoids all of the problems discussed above. The difficulties associated with wave-vector dependent crystal orbitals are side-stepped by solving the SCF equations for the crystal density matrix directly. The molecular character of these crystals is used to advantage through the application of SCF perturbation theory [13] and matrix partitioning methods. Specifically, the theory treats a molecular crystal as a lattice of properly oriented but non-interacting molecules to the zeroth order approximation and then allows for intermolecular interaction by means of high order SCF perturbation theory [13]. An important feature of this theory is that it can be applied not only to regular crystals, but also to the calculation of the properties of lattice molecules in the vicinity of lattice defects or crystal surfaces.

The original derivation of this theory was within the framework of an approximate molecular scheme. We now rederive it in terms of non-empirical single determinant molecular orbital theory.

2. Theoretical Section

In this section we discuss a solution of Roothaan's SCF matrix equation [14] for a molecular crystal. We begin by introducing the SCF matrix equations in the conventional notation suited to the theory of finite molecules. This notation is then adapted to the present application through the introduction of matrix partitioning and, by invoking the crystal's translational symmetry, through the introduction of lattice sums into the Fock operator. Finally, the intermolecular perturbation is introduced, and a method is presented for calculating the crystal density matrix.

We begin with Roothaan's SCF matrix equation for the crystal:

$$FC = SCE \tag{1}$$

where F is the Fock matrix for the entire crystal, referred to a basis set of atomic orbitals centered on the atoms of all lattice molecules. C is the coefficient matrix for the expansion of the crystal orbitals in terms of these atomic orbitals, S is the overlap matrix and E the orbital energy matrix. The energies on the diagonal of this matrix constitute the band structure for the crystal. The crystal orbitals are normalized through the matrix equation

$$\tilde{C}SC = 1 . \tag{2}$$

The crystal density matrix, P, is given by

$$P_{\mu\nu} = 2 \sum_{i}^{\text{occ}} C_{\mu i} C_{\nu i} \tag{3}$$

where μ and ν label atomic orbitals, and the summation over i includes all occupied crystal orbitals. The crystal Fock matrix is given by

$$F = H + G \tag{4}$$

where the Hamiltonian matrix, H, is given by

$$H_{\mu\nu} = (\mu| -\tfrac{1}{2}\nabla^2 |\nu) - \sum_{\beta} Z_\beta (\mu| R_\beta^{-1} |\nu) \tag{5}$$

Z_β is the nuclear charge on the βth atom, and the summation over β includes all the atoms in the crystal.

$$(\mu| -\tfrac{1}{2}\nabla^2 |\nu) = -\tfrac{1}{2} \int \chi_\mu(1) \nabla_1^2 \chi_\mu(1) d\tau_1 , \tag{6}$$

$$(\mu| R_\beta^{-1} |\nu) = \int \chi_\mu(1) R_{\beta 1}^{-1} \chi_\nu(1) d\tau_1 , \tag{7}$$

where we have assumed that all the atomic basis function, χ, are real. The electron repulsion matrix, G, is given by

$$G_{\mu\nu} = \sum_{\sigma} \sum_{\lambda} P_{\sigma\lambda} \{(\mu\nu|\sigma\lambda) - \tfrac{1}{2}(\mu\lambda|\sigma\nu)\} \tag{8}$$

where the double summations over σ and λ are over all atomic orbitals in the crystal basis set.

$$(\mu\nu|\sigma\lambda) = \int\int \chi_\mu(1) \chi_\nu(1) r_{12}^{-1} \chi_\sigma(2) \chi_\lambda(2) d\tau_1 d\tau_2 . \tag{9}$$

The method to be developed here allows calculation of the crystal density matrix rather than the crystal orbitals. This matrix is built up block by block by calculating density submatrices. Considerable clarification of this procedure can be achieved if it is assumed at the outset that the crystal basis set has been ordered so that all atomic orbitals belonging to a given molecule occur as a group in the list of basis functions [8, 11]. Under this arrangement all of the matrices occurring in the theory can be partitioned into submatrices. Those submatrices found along the diagonal are termed intramolecular because they are composed of matrix elements between atomic orbitals associated with a single molecule [8, 11]. Submatrices from the off-diagonal positions, on the other hand, are termed intermolecular because their elements are between atomic orbitals centred on two separate molecules. If we assume that there is only one molecule per unit cell, a single label is sufficient to identify a given lattice molecule. Accordingly, a submatrix of a given crystal matrix, M, may be denoted by [11]:

$${}^{TW}M = ({}^{TW}M_{\mu\nu}) \tag{10}$$

where ${}^{TW}M_{\mu\nu}$ is the matrix element between the μth atomic orbital of the molecule in the Tth unit cell and the νth orbital of the molecule in the Wth cell. It is important to recognize the vector character of these unit cell identifiers. Although this notation can readily be generalized [11] to include the many molecule complex unit cell, such a generalization would only obscure the presentation.

The Hamiltonian submatrices are written as

$${}^{TW}H_{\mu\nu} = (\mu_T| -\tfrac{1}{2}\nabla^2 |\nu_W) - \sum_{X}^{\text{u.c.}} \sum_{\beta} {}^{X}Z_\beta (\mu_T| {}^{X}R_\beta^{-1} |\nu_W) \tag{11}$$

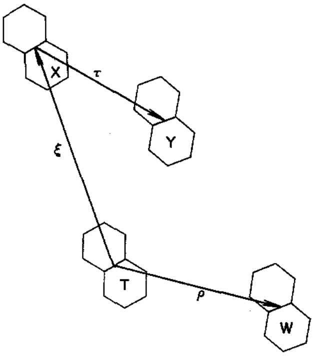

Fig. 1. Relative vector labels for molecules in a crystal lattice. Here T is the reference molecule

where X is summed over all unit cells (molecules), β is summed over all atoms of the X^{th} molecule, and μ_T is the μ^{th} atomic orbital centred on the T^{th} molecule. At this point, it is convenient to begin the introduction of the crystal's translational symmetry. Because of this symmetry, any two submatrices of a given matrix, M, will be equal if the difference between their unit cell identifiers are equal:

$$^{XY}M = {}^{TW}M \tag{12}$$

if

$$Y - X = W - T. \tag{13}$$

Such submatrices may be said to be translationally equivalent. Thus, in order to avoid duplication, it is appropriate to identify the sub-matrices by means of relative vector labels, such as those shown in Fig. 1, in preference to the absolute T, W labels. Moreover, since all the lattice molecules are symmetry related, the X label on $^{X}Z_\beta$ is redundant; it may therefore be discarded and the summation over β referred to an arbitrary lattice molecule. Under these conditions, the order of summation can be interchanged and the Z taken out of the X summation in Eq. (11), to permit the last term to be expressed in terms of a lattice sum, V:

$$^{\varrho}H_{\mu\nu} = (\mu_T| -\tfrac{1}{2}\nabla^2 |\nu_{T+\varrho}) - \delta_{d,\varrho} \sum_{\beta} Z_\beta (\mu_T | {}^{T}R_\beta^{-1} | \nu_T) - {}^{\varrho}V_{\mu\nu} \tag{14}$$

where T labels an arbitrary lattice molecule. The vector ϱ is that shown in Fig. 1, d (diagonal) corresponds to the null vector ($\varrho = 0$) and δ is the Kronecker δ.

$$^{\varrho}V_{\mu\nu} = \sum_{\beta} Z_\beta \sum_{\zeta}{}' (\mu_T | {}^{\zeta}R_\beta^{-1} | \nu_{T+\varrho}) . \tag{15}$$

ζ is the vector shown in Fig. 1, and the prime on the summation is to omit the origin term $\zeta = 0$ if $\varrho = 0$.

Similarly, the G submatrix is given by

$$^{TW}G_{\mu\nu} = \sum_{X} \sum_{Y} \sum_{\sigma} \sum_{\lambda} {}^{XY}P_{\sigma\lambda} \{(\mu_T \nu_W | \sigma_X \lambda_Y) - \tfrac{1}{2}(\mu_T \lambda_Y | \sigma_X \nu_W)\} \tag{16}$$

where the summations over σ and λ are over basis functions of molecules X and Y, respectively. The G and P submatrices can also be written in the relative label notation introduced above and the summations over X and Y equivalently replaced by summations over τ and ζ, Fig. 1. Applying the translational symmetry argument to the expression in the curly brackets of Eq. (16), we find that the integrals depend only on the three vectors, ϱ, ζ, and τ shown in Fig. 1. Thus, we introduce the following notation:

$$ {}^{\varrho}M^{(\tau,\zeta)}_{\mu\nu:\sigma\lambda} = \{(\mu_T \nu_W | \sigma_X \lambda_Y) - \tfrac{1}{2}(\mu_T \lambda_Y | \sigma_X \nu_W)\} \tag{17} $$

so that

$$ {}^{\varrho}G_{\mu\nu} = \sum_{\tau}\sum_{\zeta}\sum_{\sigma}\sum_{\lambda} {}^{\tau}P_{\sigma\lambda}\, {}^{\varrho}M^{(\tau,\zeta)}_{\mu\nu:\sigma\lambda} \tag{18} $$

Noting that ${}^{\tau}P_{\sigma\lambda}$ is independent of ζ, we may write

$$ {}^{\varrho}G_{\mu\nu} = \sum_{\tau}\sum_{\sigma}\sum_{\lambda} {}^{\tau}P_{\sigma\lambda} \sum_{\zeta} {}^{\varrho}M^{(\tau,\zeta)}_{\mu\nu:\sigma\lambda}\,. \tag{19} $$

The last summation in (19) may be considered as a separate lattice sum, ${}^{\varrho}\Gamma^{(\tau)}_{\mu\nu:\sigma\lambda}$:

$$ {}^{\varrho}\Gamma^{(\tau)}_{\mu\nu:\sigma\lambda} = \sum_{\zeta}{}' \, {}^{\varrho}M^{(\tau,\zeta)}_{\mu\nu:\sigma\lambda} \tag{20} $$

where the prime excludes $\zeta = 0$ if both ϱ and $\tau = 0$. The electron repulsion submatrix may now be written:

$$ {}^{\varrho}G_{\mu\nu} = \delta_{d,\varrho} \sum_{\sigma}\sum_{\lambda} {}^{d}P_{\mu\nu}\, {}^{d}M^{(d,d)}_{\mu\nu:\sigma\lambda} + \sum_{\tau}\sum_{\sigma}\sum_{\lambda} {}^{\tau}P_{\sigma\lambda}\, {}^{\varrho}\Gamma^{(\tau)}_{\mu\nu:\sigma\lambda}\,. \tag{21} $$

3. Definition of the Fock Perturbation Submatrices

We begin by expanding the SCF matrix equation for the crystal in a perturbation series,

$$ \begin{aligned} &(F^{(0)} + F^{(1)} + F^{(2)} + \cdots)(C^{(0)} + C^{(1)} + C^{(2)} + \cdots) \\ &= (S^{(0)} + S^{(1)} + S^{(2)} + \cdots)(C^{(0)} + C^{(1)} + C^{(2)} + \cdots)\cdot(E^{(0)} + E^{(1)} + E^{(2)} + \cdots) \end{aligned} \tag{22} $$

which is solved by the method given in the Appendix. In order to take advantage of the molecular character of molecular crystals, the zero order solutions are taken to be the molecular orbitals of correctly oriented but hypothetically non-interacting lattice molecules [8, 11]. Accordingly, both $F^{(0)}$ and $S^{(0)}$ are block diagonal [8, 11]. The diagonal blocks are the appropriate free molecule matrices from each individual lattice molecule. Thus, unless $\varrho = d$, both ${}^{\varrho}F^{(0)}$ and ${}^{\varrho}S^{(0)}$ are zero. The diagonal zero order Fock submatrices are given by

$$ {}^{d}F^{(0)}_{\mu\nu} = (\mu_T | -\tfrac{1}{2}\nabla^2 | \nu_T) - \sum_{\beta} Z_{\beta}(\mu_T | {}^{T}R_{\beta}^{-1} | \nu_T) + \sum_{\sigma}\sum_{\lambda} {}^{d}P^{(0)}_{\sigma\lambda}\, {}^{d}M^{(d,d)}_{\mu\nu:\sigma\lambda}\,. \tag{23} $$

T labels an arbitrarily chosen lattice molecule, and ${}^{d}P^{(0)}$, the density matrix for an isolated lattice molecule, is a zero order density submatrix from the diagonal of $P^{(0)}$.

$$ {}^{d}P^{(0)}_{\mu\nu} = 2 \sum_{i}^{\mathrm{occ}} {}^{T}C^{(0)}_{\mu i}\, {}^{T}C^{(0)}_{\nu i}\,. \tag{24} $$

Note, $P^{(0)}$ is block diagonal as are all other zero order matrices. The summation is over the occupied orbitals of the T^{th} molecule. ${}^{T}C^{(0)}_{\mu i}$ is the coefficient of the μ^{th}

atomic orbital in the i^{th} molecular orbital localized on the T^{th} molecule to the zeroth order.

We now consider the definition of the perturbation operators to all orders. The form of the full crystal Fock and Hamiltonian operators and our choice of zero order solution allows considerable latitude in the definition of the perturbation operators. In order to optimize the convergence of the perturbation expansion, we include two contributions in the first order Fock operators. The first is the static field arising from the zero order charge distribution in the lattice. The second is the first order polarization field arising from the effect of the static field on the molecules. Thus, by definition,

$$\begin{aligned} {}^{\varrho}F^{(1)}_{\mu\nu} &= (1-\delta_{d,\varrho})\,(\mu_T| -\tfrac{1}{2}\nabla^2 | \nu_{T+\varrho}) - {}^{\varrho}V_{\mu\nu} + \sum_{\sigma}\sum_{\lambda} {}^{d}P^{(0)}_{\sigma\lambda}\, {}^{\varrho}\Gamma^{(d)}_{\mu\nu:\sigma\lambda} \\ &+ \delta_{d,\varrho}\sum_{\sigma}\sum_{\lambda} {}^{d}P^{(1)}_{\sigma\lambda}\, {}^{d}M^{(d,d)}_{\mu\nu:\sigma\lambda} + \sum_{\tau}\sum_{\sigma}\sum_{\lambda} {}^{\tau}P^{(1)}_{\sigma\lambda}\, {}^{\varrho}\Gamma^{(\tau)}_{\mu\nu:\sigma\lambda}\,. \end{aligned} \tag{25}$$

Under this definition of $F^{(0)}$ and $F^{(1)}$ all Hamiltonian matrix elements are accounted for, and so ${}^{\varrho}H^{(n)}=0$ if $n>1$. Thus, all remaining higher order Fock submatrices contain only polarization terms. Therefore, the n^{th} order Fock submatrix is given by:

$${}^{\varrho}F^{(n)}_{\mu\nu} = \delta_{d,\varrho}\sum_{\sigma}\sum_{\lambda} {}^{d}P^{(n)}_{\sigma\lambda}\, {}^{\varrho}M^{(d,d)}_{\mu\nu:\sigma\lambda} + \sum_{\tau}\sum_{\sigma}\sum_{\lambda} {}^{\tau}P^{(n)}_{\sigma\lambda}\, {}^{\varrho}\Gamma^{(\tau)}_{\mu\nu:\sigma\lambda}\,. \tag{26}$$

4. Calculation of the Crystal Density Matrix

The perturbation equation, Eq. (23), is solved for $P^{(1)}$ and $P^{(2)}$ by the method derived in the Appendix. It is assumed that $P^{(0)}$ has already been determined by means of a conventional SCF calculation on a chosen reference lattice molecule. The final density matrix is given, of course, by the sum of $P^{(0)}$, $P^{(1)}$, and $P^{(2)}$. The crystal density matrix cannot be handled as a single entity, and so the expressions for $P^{(1)}$ and $P^{(2)}$ are partitioned into submatrix equations. Each resulting density submatrix equation is solved separately, but not independently. The density matrix for the crystal is, thus, built-up block by block through the calculation of density submatrices.

The crystal symmetry drastically reduces the number of submatrices required for the complete specification of the crystal density matrix, since only *translationally inequivalent* submatrices need be calculated. In the present case of one molecule per unit cell, all that is required is a single intramolecular submatrix and one set of intermolecular submatrices, involving an arbitrarily chosen reference molecule and the remainder of the lattice. Fortunately, relatively few intermolecular matrices will have to be calculated since, for molecular crystals at least, ${}^{\varrho}P$ will tend strongly to zero as $|\varrho|$ increases. The presence of any point group symmetry in the lattice would further reduce the number of submatrices to be calculated.

Expressions for the first and second order density matrices are given in the appendix. These equations are now partitioned into submatrix equations. We start with the first order density matrix, $P^{(1)}$:

$$P^{(1)}_{\mu\nu} = 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{all}} \mathfrak{A}_{ki}\{C^{(0)}_{\mu i}\,C^{(0)}_{\nu k} + C^{(0)}_{\mu k}\,C^{(0)}_{\nu i}\}\,. \tag{27}$$

The summations in the unpartitioned form of the equation are over crystal orbitals. If both i and k are occupied

$$\mathfrak{A}_{ki} = -\tfrac{1}{2} S^{(1)}_{ki} \tag{28}$$

and if i is occupied and k vacant

$$\mathfrak{A}_{ki} = \mathfrak{F}^{(1)}_{ki} / (\varepsilon^{(0)}_i - \varepsilon^{(0)}_k) \,. \tag{29}$$

Here

$$\mathfrak{F}^{(1)}_{ki} = F^{(1)}_{ki} - S^{(1)}_{ki}\, \varepsilon^{(0)}_i \,. \tag{30}$$

$F^{(1)}_{ki}$ and $S^{(1)}_{ki}$ are defined in the Appendix.

The full crystal density matrix may be partitioned into submatrices by making use of the prescribed ordering of the basis set and the block diagonal form of the $C^{(0)}$ matrix. The submatrix between molecules T and W is given by

$${}^{TW}P^{(1)}_{\mu\nu} = 2 \sum_i^{\mathrm{occ}_T} \sum_k^{\mathrm{all}_W} {}^{WT}\mathfrak{A}_{ki}\, {}^{T}C^{(0)}_{\mu i}\, {}^{W}C^{(0)}_{\nu k} + 2 \sum_i^{\mathrm{occ}_W} \sum_k^{\mathrm{all}_T} {}^{TW}\mathfrak{A}_{ki}\, {}^{T}C^{(0)}_{\mu k}\, {}^{W}C^{(0)}_{\nu i} \,. \tag{31}$$

The orbital summations in this equation are now over molecular orbitals associated with either molecule W or T. ${}^{WT}\mathfrak{A}$ is the W, T^{th} submatrix of $\mathfrak{A}$. At this point we can again involve the crystal translational symmetry. As discussed above, it is clearly unnecessary to calculate the density submatrices for every value of T and W since they depend only on ϱ, the difference between T and W. Thus,

$${}^{\varrho}P^{(1)}_{\mu\nu} = 2 \sum_i^{\mathrm{occ}} \sum_k^{\mathrm{all}} ({}^{\bar{\varrho}}\mathfrak{A}_{ki}\, C^{(0)}_{\mu i}\, C^{(0)}_{\nu k} + {}^{\varrho}\mathfrak{A}_{ki}\, C^{(0)}_{\mu k}\, C^{(0)}_{\nu i}) \,. \tag{32}$$

The summations are now over the molecular orbitals of an arbitrary lattice molecule. If, for example, k and i label vacant and occupied orbitals, respectively:

$${}^{TW}\mathfrak{A}_{ki} = {}^{\varrho}\mathfrak{A}_{ki} = ({}^{\varrho}F^{(1)}_{ki} - {}^{\varrho}S^{(1)}_{ki}\, \varepsilon^{(0)}_i)/(\varepsilon^{(0)}_i - \varepsilon^{(0)}_k) \,. \tag{33}$$

Since, in the present case, all lattice molecules are equivalent, labelling of the zero order orbital energies with regard to their molecular origin is unnecessary.

$${}^{\varrho}F^{(1)}_{ki} = \sum_\mu \sum_\nu C^{(0)}_{\mu k}\, C^{(0)}_{\nu i}\, {}^{\varrho}F^{(1)}_{\mu\nu} \tag{34}$$

where ${}^{\varrho}F^{(1)}_{\mu\nu}$ is defined in Eq. (25). Once more the equivalence of the molecules makes labelling of the molecular orbital coefficients with regard to their molecular origin unnecessary. The summations over μ and ν are over all the atomic orbitals associated with a single molecule in the lattice. Note,

$${}^{\bar{\varrho}}\mathfrak{A} = {}^{WT}\mathfrak{A} \,. \tag{35}$$

Equation (32), in conjunction with Eqs. (28) and (29), constitutes the first order solution to the crystal SCF matrix equation.

The second order density matrix is given by

$$P^{(2)}_{\mu\nu} = 2 \sum_i^{\mathrm{occ}} \sum_k^{\mathrm{all}} \mathfrak{B}_{ki} (C^{(0)}_{\mu i}\, C^{(0)}_{\nu k} + C^{(0)}_{\mu k}\, C^{(0)}_{\nu i}) + 2 \sum_i^{\mathrm{occ}} \sum_k^{\mathrm{vac}} \sum_l^{\mathrm{vac}} A_{ki}\, A_{li}\, C^{(0)}_{\mu k}\, C^{(0)}_{\nu l} \tag{36}$$

where, $\mathfrak{B}_{ki}$ is defined in the appendix. On partitioning (36) into density submatrices, making use of the block diagonal form of $C^{(0)}$, we find

$$\begin{aligned}{}^{TW}P^{(2)}_{\mu\nu} = {} & 2 \sum_{i}^{\mathrm{occ}_W} \sum_{k}^{\mathrm{all}_T} {}^{TW}\mathfrak{B}_{ki}\, {}^{T}C^{(0)}_{\mu k}\, {}^{W}C^{(0)}_{\nu i} + 2 \sum_{i}^{\mathrm{occ}_T} \sum_{k}^{\mathrm{all}_W} {}^{WT}\mathfrak{B}_{ki}\, {}^{W}C^{(0)}_{\nu k}\, {}^{T}C^{(0)}_{\mu i} \\ & + 2 \sum_{X}^{\mathrm{u.c.}} \sum_{i}^{\mathrm{occ}_X} \sum_{k}^{\mathrm{vac}_T} \sum_{l}^{\mathrm{vac}_W} {}^{TX}A_{ki}\, {}^{WX}A_{li}\, {}^{T}C^{(0)}_{\mu k}\, {}^{W}C^{(0)}_{\nu l} \,.\end{aligned} \tag{37}$$

The appearance of a triple summation in the expression for $P^{(2)}$ leads to a lattice summation, $\Sigma_X^{\mathrm{u.c.}}$, in the final partitioned expression for the density submatrix. Once more the notation is simplified through the introduction of the relative unit cell identifiers of Fig. 1

$$\begin{aligned}{}^{\varrho}P^{(2)}_{\mu\nu} = {} & 2 \sum_{i}^{\mathrm{occ}} \sum_{k}^{\mathrm{all}} \left({}^{\varrho}\mathfrak{B}_{ki}\, C^{(0)}_{\mu k}\, C^{(0)}_{\nu i} + {}^{\bar{\varrho}}\mathfrak{B}_{ki}\, C^{(0)}_{\mu i}\, C^{(0)}_{\nu k} \right) \\ & + 2 \sum_{\zeta} \sum_{i}^{\mathrm{occ}} \sum_{k}^{\mathrm{vac}} \sum_{l}^{\mathrm{vac}} {}^{\zeta}A_{ki}\, {}^{(\zeta-\varrho)}A_{li}\, C^{(0)}_{\mu k}\, C^{(0)}_{\nu l} \,.\end{aligned} \tag{38}$$

As the lattice molecules are all the same, it is unnecessary to label the zero order molecular orbitals with respect to their molecular origin. Fortunately, for molecular crystals, at least, the geometry of the molecular packing in the crystal is such that very few terms need be included in the ζ summation [11].
From the Appendix, if both i and k label occupied orbitals

$${}^{\varrho}\mathfrak{B}_{ki} = -\tfrac{1}{2} \sum_{X} \left[\sum_{l}^{\mathrm{vac}} {}^{WX}A_{il}\, {}^{TX}A_{kl} - \sum_{l}^{\mathrm{all}} {}^{WX}S^{(1)}_{il}\, {}^{XT}S^{(1)}_{lk} \right] . \tag{39}$$

X sums over all unit cells in the crystal. We have chosen to set $S^{(2)} = 0$. Equation (39) may be written

$${}^{\varrho}\mathfrak{B}_{ki} = -\tfrac{1}{2} \sum_{\zeta} \left[\sum_{l}^{\mathrm{vac}} {}^{(\zeta-\varrho)}A_{il}\, {}^{\zeta}A_{kl} - \sum_{l}^{\mathrm{all}} {}^{(\zeta-\varrho)}S^{(1)}_{il}\, {}^{\bar{\zeta}}S^{(1)}_{lk} \right] \tag{40}$$

where the vector ζ is defined in Fig. 1. Similarly, if i is occupied and k vacant, from Eq. (48 A) of the Appendix,

$$\begin{aligned}{}^{\varrho}\mathfrak{B}_{ki} = {} & {}^{\varrho}\mathfrak{F}^{(2)}_{ki} / (\varepsilon^{(0)}_i - \varepsilon^{(0)}_k) + \Bigg[\sum_{\zeta} \Bigg(\sum_{l}^{\mathrm{vac}} {}^{\zeta}\mathfrak{F}^{(1)}_{kl}\, {}^{(\varrho-\zeta)}A_{li} - \sum_{l}^{\mathrm{occ}} {}^{\zeta}A_{kl}\, {}^{(\varrho-\zeta)}\mathfrak{F}^{(1)}_{li} \\ & - \sum_{l}^{\mathrm{all}} {}^{\zeta}S^{(1)}_{kl}\, {}^{(\varrho-\zeta)}\mathfrak{F}^{(1)}_{li} \Bigg) \Bigg] \Big/ (\varepsilon^{(0)}_i - \varepsilon^{(0)}_k) - \sum_{l}^{\mathrm{occ}} {}^{\zeta}A_{kl}\, {}^{(\zeta-\varrho)}S^{(1)}_{il} \,.\end{aligned} \tag{41}$$

Equation (38) in conjunction with Eqs. (40) and (41), constitutes the second order solution to the crystal SCF equation.

Assuming that all of the required integrals and lattice sums for the problem have been evaluated, the method of calculation is as follows. The first step is the solution of the zero order equation for an arbitrary lattice molecule to obtain the zero order molecular orbitals and orbital energies. The next step is the calculation of all the required first order density submatrices, Eq. (32). These are solved as coupled equations, since the calculation of any given ${}^{\varrho}F^{(1)}$ requires all nonnegligible ${}^{\zeta}P^{(1)}$. Each ${}^{\tau}P^{(1)}$ that contributes to the ${}^{\varrho}F^{(1)}$ submatrices is calculated from an intermolecular density submatrix equation. Even if density submatrices involving next nearest neighbour molecules are calculated, only about eight equations have to be solved [11]. Moreover, the presence of an n-fold axis in the crystal point group would reduce this number by a factor of n. Once the first order equations have been solved the $S^{(1)}$ submatrices are used in conjunction with the resultant A and $\mathfrak{F}^{(1)}$ submatrices to calculate the constant, non-iterative, components of the $P^{(2)}$ submatrices. Completion of the $P^{(2)}$ calculation again requires the iterative solution of several matrix equations, Eq. (38).

It is important to realize that the density matrices calculated by the above method explicitly include multimolecular interactions through the presence of the Coulomb lattice sums in the $F^{(n)}$ submatrices and three molecule interactions through the presence of lattice sums in the expressions for $\mathfrak{B}$, Eqs. (40) and (41).

The energy per mole, W, of the crystal may readily be calculated from the various submatrices as follows [11]. Let W' be the extensive energy of the crystal, then

$$W' = \tfrac{1}{2}\sum_{\mu}\sum_{\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + \text{nuclear repulsion}\,, \tag{42}$$

$$= \tfrac{1}{2}\sum_{T}\sum_{W}\sum_{\mu}^{T}\sum_{\nu}^{W} {}^{TW}P_{\mu\nu}({}^{TW}H_{\mu\nu} + {}^{TW}F_{\mu\nu}) + N.R.'\,, \tag{43}$$

where $N.R.'$ is the total nuclear repulsion energy.

If N is the number of unit cells, then applying the translational symmetry argument,

$$W' = \tfrac{1}{2}N\sum_{\varrho}\sum_{\mu}\sum_{\nu} {}^{\varrho}P_{\mu\nu}({}^{\varrho}H_{\mu\nu} + {}^{\varrho}F_{\mu\nu}) + N.R.'\,. \tag{44}$$

Dividing by N to obtain the energy per unit cell, we find

$$W = \tfrac{1}{2}\sum_{\varrho}\sum_{\mu}\sum_{\nu} {}^{\varrho}P_{\mu\nu}({}^{\varrho}H_{\mu\nu} + {}^{\varrho}F_{\mu\nu}) + N.R. \tag{45}$$

To estimate the crystal binding energy per molecule, we calculate the average energy per molecule in the crystal and subtract from it the energy of an isolated molecule, given here by

$$\tfrac{1}{2}\sum_{\mu}\sum_{\nu} {}^{d}P^{(0)}_{\mu\nu}({}^{d}H^{(0)}_{\mu\nu} + {}^{d}F^{(0)}_{\mu\nu}) + n.r. \tag{46}$$

where $n.r.$ is the nuclear repulsion energy for a single molecule.

The perturbation series for the average energy per molecule in the crystal is simplified by the block diagonal form of the zero order matrices and by the fact that

$$\sum_{\mu}\sum_{\nu} {}^{\varrho}P^{(1)}_{\mu\nu}\,{}^{\varrho}F^{(0)}_{\mu\nu} = 0\,. \tag{47}$$

The final result for the binding energy per molecule, ΔW, is

$$\begin{aligned}\Delta W = {} & \tfrac{1}{2}\sum_{\mu}\sum_{\nu}\{{}^{d}P^{(0)}_{\mu\nu}\{{}^{d}H^{(1)}_{\mu\nu} + {}^{d}F^{(1)}_{\mu\nu}\} + {}^{d}P^{(1)}_{\mu\nu}\,{}^{d}H^{(0)}_{\mu\nu} \\ & + {}^{d}P^{(1)}_{\mu\nu}\{{}^{d}H^{(1)}_{\mu\nu} + {}^{d}F^{(1)}_{\mu\nu}\} + {}^{d}P^{(0)}_{\mu\nu}\,{}^{d}F^{(2)}_{\mu\nu} + {}^{d}P^{(2)}_{\mu\nu}({}^{d}H^{(0)}_{\mu\nu} + {}^{d}F^{(0)}_{\mu\nu})\} \\ & + \tfrac{1}{2}\sum_{\varrho}\sum_{\mu}\sum_{\nu}[{}^{\varrho}P^{(1)}_{\mu\nu}({}^{\varrho}H^{(1)}_{\mu\nu} + {}^{\varrho}F^{(1)}_{\mu\nu}) + {}^{\varrho}P^{(2)}_{\mu\nu}({}^{\varrho}H^{(1)}_{\mu\nu} + {}^{\varrho}F^{(1)}_{\mu\nu}) + {}^{\varrho}P^{(1)}_{\mu\nu}\,{}^{\varrho}F^{(2)}_{\mu\nu}] + N.R.\end{aligned} \tag{48}$$

where $N.R.$ now only includes intermolecular repulsion terms.

Although the calculations discussed here have been taken to the second order, the last terms in Eq. (48) combine first and second order contributions to yield terms that are overall of the third order. This procedure would be inconsistent in the calculation of molecular interaction constants, for example, but it is acceptable in the present application since the choice of perturbation is, to some extent, arbitrary. The inclusion of the last terms is recommended since studies with perturbation calculations based on semi-empirical MO theories showed that their inclusion improved the performance of the theory to the point where it could be confidently employed for the calculation of molecular configurations [7] within dimers.

As calculated in Eq. (48), the binding energy contains all of the interactions included in the single determinant SCF theory. Thus, the present method includes contributions from intermolecular electron exchange, intermolecular charge transfer, together with the major terms which can be derived from classical electrostatic theory. The latter include direct multipole-multipole interactions together with the corresponding polarization forces. Dispersion forces, which arise from Coulomb electron correlation, are not included and must be considered separately. The theory can confidently be applied to hydrogen bonded and charge transfer crystals. Useful insights can also be obtained for molecular crystals where dispersion energies make a substantial contribution to the binding energy.

5. Discussion

A method has been developed in the previous section, for solving Roothaan's SCF matrix equation for an infinite molecular crystal. This approach brings simple molecular crystals within range of *ab initio* molecular orbital calculations. It also presents an opportunity to study intermolecular forces within physically realizable systems that are available for experimental study. These calculations should also provide valuable insight into the electronic processes within molecular crystals.

The above theory has been successfully applied at the semiempirical level to several molecular crystals [8–12]. The convergence of the perturbation series was monitored by calculating the complete third order together with part of the fourth order energy [11]. These calculations suggest that the procedure recommended here, the calculation of P to second order with the energy taken partially to third order, should be adequate for most simple molecular crystals. Crystals composed of unusually strongly interacting molecules, such as those postulated for charge transfer crystals [15], may require the calculation of $P^{(3)}$ in order to obtain acceptably accurate results. But even here, the second order calculations should provide extremely valuable results at the semi-quantitative level.

The program [16] available for the semi-empirical version of the theory should greatly facilitate the implementation of the *ab initio* theory. The solution of the perturbation equations for the lattice molecules is the same in both theories, apart from changes in the definitions of $\mathfrak{F}$, $\mathfrak{A}$, and $\mathfrak{B}$. Thus, the existing computer program, PREDEN/CRYDEN [16], could be adapted to *ab initio* calculations by the incorporation of the necessary integral packages and the modification of the

Fock submatrix algorithms. The overlay structure of the program would lend itself to this process.

Finally, the theory developed here assumes an ideal symmetry for the crystal lattice. However, should this symmetry be lowered or completely removed by the presence of a lattice defect or the proximity of a surface, the general method of approach would still be valid. The effect of each reduction of symmetry is to increase the number of distinguishable density submatrices that must be calculated. A method for treating this problem has been discussed by Crowe and Santry [17] for the semi-empirical version of the theory.

Appendix

We briefly review here the derivation of the first and second order contributions to the density matrix as calculated by SCF perturbation theory. We start with the Roothaan SCF matrix equation [14],

$$FC = SCE \tag{1A}$$

which is expanded in a perturbational series, here limited to the second order:

$$\begin{aligned}(F^{(0)}+F^{(1)}+F^{(2)}+\cdots)(C^{(0)}+C^{(1)}+C^{(2)}+\cdots) &= (S^{(0)}+S^{(1)}+S^{(2)}+\cdots)\\ &\quad\cdot(C^{(0)}+C^{(1)}+C^{(2)}+\cdots)(E^{(0)}+E^{(1)}+E^{(2)}+\cdots).\end{aligned} \tag{2A}$$

Collecting terms by order we find, up to the second order

$$F^{(0)}C^{(0)} = S^{(0)}C^{(0)}E^{(0)}, \tag{3A}$$

$$F^{(1)}C^{(0)} + F^{(0)}C^{(1)} = S^{(0)}C^{(0)}E^{(1)} + S^{(0)}C^{(1)}E^{(0)} + S^{(1)}C^{(0)}E^{(0)}, \tag{4A}$$

$$\begin{aligned}F^{(2)}C^{(0)} + F^{(1)}C^{(1)} + F^{(0)}C^{(2)} &= S^{(0)}C^{(0)}E^{(2)} + S^{(0)}C^{(2)}E^{(0)} + S^{(2)}C^{(0)}E^{(0)}\\ &\quad + S^{(0)}C^{(1)}E^{(1)} + S^{(1)}C^{(0)}E^{(1)} + S^{(1)}C^{(1)}E^{(0)}.\end{aligned} \tag{5A}$$

If these equations are solved subject to the constraint [14],

$$\tilde{C}SC = 1, \tag{6A}$$

E can be considered diagonal to all orders. Expanding (6A) in a perturbation series we find

$$\tilde{C}^{(0)}S^{(0)}C^{(0)} = 1, \tag{7A}$$

$$\tilde{C}^{(0)}S^{(0)}C^{(1)} + \tilde{C}^{(0)}S^{(1)}C^{(0)} + \tilde{C}^{(1)}S^{(0)}C^{(0)} = 0, \tag{8A}$$

$$\begin{aligned}&\tilde{C}^{(0)}S^{(0)}C^{(2)} + \tilde{C}^{(0)}S^{(2)}C^{(0)} + \tilde{C}^{(2)}S^{(0)}C^{(0)} + \tilde{C}^{(0)}S^{(1)}C^{(1)} + \tilde{C}^{(1)}S^{(1)}C^{(0)}\\ &\quad + \tilde{C}^{(1)}S^{(0)}C^{(1)} = 0.\end{aligned} \tag{9A}$$

It is assumed that Eq. (3A) has been solved, so that $F^{(0)}$, $C^{(0)}$, $S^{(0)}$, and $E^{(0)}$ are all known. Equation (4A) is solved by expanding $C^{(1)}$ in terms of the complete set $C^{(0)}$:

$$C^{(1)} = C^{(0)}A \tag{10A}$$

where A is a matrix of mixing coefficients. Substitute for $C^{(1)}$ in (4A) and multiply to the left by $\tilde{C}^{(0)}$:

$$F^{(1)} + E^{(0)}A = E^{(1)} + AE^{(0)} + S^{(1)}E^{(0)} \tag{11A}$$

where $F^{(1)}$ and $S^{(1)}$ are *now* referred to a basis of zero order molecular orbitals,

$$S^{(1)}_{ij} = \sum_{\mu}\sum_{\nu} C^{(0)}_{\mu i}\, S^{(1)}_{\mu\nu}\, C^{(0)}_{\nu j}\,, \tag{12A}$$

$$F^{(1)}_{ij} = \sum_{\mu}\sum_{\nu} C^{(0)}_{\mu i}\, F^{(1)}_{\mu\nu}\, C^{(0)}_{\nu j}\,. \tag{13A}$$

Define a new F matrix, Eq. (14A)

$$\mathfrak{F}^{(n)} = F^{(n)} - S^{(n)} E^{(0)} \tag{14A}$$

and substitute into (11A):

$$A E^{(0)} - E^{(0)} A = -E^{(1)} + \mathfrak{F}^{(1)}\,. \tag{15A}$$

Also, if $E^{(1)}$ is to be diagonal, from Eq. (8A),

$$A + \tilde{A} = -S^{(1)}\,. \tag{16A}$$

From (15A), if $i \neq j$

$$A_{ij} = \mathfrak{F}^{(1)}_{ij}/(\varepsilon^0_j - \varepsilon^0_i) \tag{17A}$$

and from (16A)

$$A_{ii} = -\tfrac{1}{2} S^{(1)}_{ii}\,. \tag{18A}$$

Now that A has been derived, $P^{(1)}$ can be calculated:

$$\begin{aligned} P^{(1)}_{\mu\nu} &= 2 \sum_{i}^{\text{occ}} \left(C^{(0)}_{\mu i}\, C^{(1)}_{\nu i} + C^{(1)}_{\mu i}\, C^{(0)}_{\nu i}\right) \\ &= 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{all}} A_{ki} \left(C^{(0)}_{\mu i}\, C^{(0)}_{\nu k} + C^{(0)}_{\mu k}\, C^{(0)}_{\nu i}\right). \end{aligned} \tag{19A}$$

This equation is singular if the zero order solution contains degenerate orbitals. However, by making use of Eq. (16A), it can easily be reduced to a non-singular form:

$$P^{(1)}_{\mu\nu} = 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} A_{ki} \left(C^{(0)}_{\mu i}\, C^{(0)}_{\nu k} + C^{(0)}_{\mu k}\, C^{(0)}_{\nu i}\right) - 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{occ}} S^{(1)}_{ki}\, C^{(0)}_{\mu i}\, C^{(0)}_{\nu k}\,. \tag{20A}$$

This can be conveniently expressed, for later use, as

$$P^{(1)}_{\mu\nu} = 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{all}} \mathfrak{A}_{ki} \left(C^{(0)}_{\mu i}\, C^{(0)}_{\nu k} + C^{(0)}_{\mu k}\, C^{(0)}_{\nu i}\right) \tag{21A}$$

where, if both i and k are occupied

$$\mathfrak{A}_{ki} = -\tfrac{1}{2} S^{(1)}_{ki} \tag{22A}$$

and if i is occupied and k vacant

$$\mathfrak{A}_{ki} = \mathfrak{F}^{(1)}_{ki}/(\varepsilon^{(0)}_i - \varepsilon^{(0)}_k)\,. \tag{23A}$$

Note, the $\mathfrak{A}$ matrix is neither symmetric nor skew symmetric. Equation (21A) is for all practical purposes the solution to the first order equation. It has to be calculated iteratively since the evaluation of $P^{(1)}$ requires $\mathfrak{F}^{(1)}$ which itself requires $P^{(1)}$ through $F^{(1)}$. The second order equations are solved in much the same way. $C^{(2)}$ is expanded in terms of $C^{(0)}$:

$$C^{(2)} = C^{(0)} B\,. \tag{24A}$$

This is substituted into Eq. (5A) which, on multiplying to the left by $\tilde{C}$, yields

$$E^{(0)}B - BE^{(0)} = -\mathfrak{F}^{(2)} - \mathfrak{F}^{(1)}A + E^{(2)} + AE^{(1)} + S^{(1)}\mathfrak{F}^{(1)}. \qquad (25\mathrm{A})$$

The following equation, derived from (15A), has been used in the derivation of (25A).

$$S^{(1)}E^{(1)} + S^{(1)}AE^{(0)} = S^{(1)}\mathfrak{F}^{(1)} + S^{(1)}E^{(0)}A. \qquad (26\mathrm{A})$$

The matrices in Eq. (25A) are, as for the first order equation, referred to a basis of zero order molecular orbitals. The second order ortho-normality equation, (9A), yields directly on substitution for $C^{(1)}$ and $C^{(2)}$:

$$B + \tilde{B} = -S^{(2)} - S^{(1)}A - \tilde{A}S^{(1)} - \tilde{A}A. \qquad (27\mathrm{A})$$

Noting, from Eq. (16A), that

$$A\tilde{A} = -AA - AS^{(1)}, \qquad (28\mathrm{A})$$

equation (27A) can be written in the more useful form

$$B + \tilde{B} = -S^{(2)} + S^{(1)}S^{(1)} - A\tilde{A}. \qquad (29\mathrm{A})$$

If B is constrained to satisfy this orthogonality condition $E^{(2)}$ can be assumed to be diagonal. Thus, for $k \neq i$, from (25A)

$$B_{ki} = \mathfrak{F}^{(2)}_{ki}/(\varepsilon^{(0)}_i - \varepsilon^{(0)}_k) + \left[\sum_l^{\text{all}} (\mathfrak{F}^{(1)}_{kl}A_{li} - S^{(1)}_{kl}\mathfrak{F}^{(1)}_{li}) - A_{ki}\,\varepsilon^{(1)}_{ii}\right]\Big/(\varepsilon^{(0)}_i - \varepsilon^{(0)}_k), \quad (30\mathrm{A})$$

and

$$B_{ii} = -\tfrac{1}{2}\left\{S^{(2)}_{ii} - \sum_l^{\text{all}} (S^{(1)}_{il}S^{(1)}_{li} - A_{il}A_{il})\right\}. \qquad (31\mathrm{A})$$

Now that B has been derived, the next step is to calculate the second order change in the density matrix, $P^{(2)}$

$$P^{(2)}_{\mu\nu} = 2\sum_i^{\text{occ}} \{C^{(1)}_{\mu i}C^{(1)}_{\nu i} + C^{(0)}_{\mu i}C^{(2)}_{\nu i} + C^{(2)}_{\mu i}C^{(0)}_{\nu i}\} \qquad (32\mathrm{A})$$

which, on substituting for $C^{(1)}$ and $C^{(2)}$, becomes

$$P^{(2)}_{\mu\nu} = 2\sum_i^{\text{occ}}\sum_k^{\text{all}}\sum_l^{\text{all}} A_{ki}A_{li}C^{(0)}_{\mu k}C^{(0)}_{\nu l} + 2\sum_i^{\text{occ}}\sum_k^{\text{all}} B_{ki}(C^{(0)}_{\mu i}C^{(0)}_{\nu k} + C^{(0)}_{\mu k}C^{(0)}_{\nu i}). \quad (33\mathrm{A})$$

This expression is singular and thus cannot be used for calculations where the zero order orbitals are degenerate. These singularities, however, can be easily combed out by the following manipulations. Consider the two contributions to $P^{(2)}$ in Eq. (33A) separately, taking the first term first:

$$\text{First term} = 2\left[\sum_i^{\text{occ}}\sum_k^{\text{occ}}\sum_l^{\text{occ}} + \sum_i^{\text{occ}}\sum_k^{\text{vac}}\sum_l^{\text{occ}} + \sum_i^{\text{occ}}\sum_k^{\text{occ}}\sum_l^{\text{vac}} + \sum_i^{\text{occ}}\sum_k^{\text{vac}}\sum_l^{\text{vac}}\right] A_{ki}A_{li}C^{(0)}_{\mu k}C^{(0)}_{\nu l}. \quad (34\mathrm{A})$$

Of all these terms only the fourth is non-singular. The objective is to find contributions from the second term of (33A) which will either cancel or combine with terms in (34A) to yield a final overall non-singular expression.

$$\text{Second term} = 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{vac}} B_{ki}g_{ik} + 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{occ}} (B_{ik}+B_{ki})\, C_{\mu i}^{(0)}C_{\nu k}^{(0)} \tag{35A}$$

where

$$g_{ik} = C_{\mu i}^{(0)}C_{\nu k}^{(0)} + C_{\mu k}^{(0)}C_{\nu i}^{(0)}\,. \tag{36A}$$

Using Eq. (29A), Eq. (35A) may be written as

$$\begin{aligned}&2\sum_{i}^{\text{occ}}\sum_{k}^{\text{vac}} B_{ki}g_{ik} + 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{occ}} C_{\mu k}^{(0)}C_{\nu i}^{(0)}\left(\sum_{l}^{\text{all}} S_{il}^{(1)}S_{lk}^{(1)} - S_{ki}^{(2)}\right)\\ &\qquad - 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{occ}}\sum_{l}^{\text{vac}} A_{il}A_{kl}C_{\mu k}^{(0)}C_{\nu i}^{(0)} - 2\sum_{i}^{\text{occ}}\sum_{k}^{\text{occ}}\sum_{l}^{\text{occ}} A_{il}A_{kl}C_{\mu k}^{(0)}C_{\nu i}^{(0)}\,.\end{aligned} \tag{37A}$$

The last term of (37A), which is singular, cancels the first term of (34A). All the remaining terms of (37A), save the first, are non-singular. The second and third terms of Eq. (34A) can be combined and rearranged to give

$$2\sum_{i}^{\text{occ}}\sum_{k}^{\text{vac}}\sum_{l}^{\text{occ}} A_{kl}A_{il}g_{ik} \tag{38A}$$

which is combined with the remaining singular term, the first, of Eq. (37A):

$$2\sum_{i}^{\text{occ}}\sum_{k}^{\text{vac}} g_{ik}\left(B_{ki} + \sum_{l}^{\text{occ}} A_{kl}A_{il}\right). \tag{39A}$$

Expand B_{ki} using Eq. (30A), Eq. (40A):

$$2\sum_{i}^{\text{occ}}\sum_{k}^{\text{vac}} g_{ik}\left[\frac{\mathfrak{F}_{ki}^{(2)}}{\varepsilon_i^{(0)}-\varepsilon_k^{(0)}} + \left(\sum_{l}^{\text{all}} \mathfrak{F}_{kl}^{(1)}A_{li} - A_{ki}\,\varepsilon_i^{(1)} - \sum_{l}^{\text{all}} S_{kl}^{(1)}\mathfrak{F}_{li}^{(1)}\right)\Big/(\varepsilon_i^{(0)}-\varepsilon_k^{(0)}) + \sum_{l}^{\text{occ}} A_{kl}A_{il}\right]. \tag{40A}$$

Combine the occupied component of the second term with the fifth term. Expand all the A's using Eq. (17A).

$$\begin{aligned}\sum_{l}^{\text{occ}}\left\{\frac{\mathfrak{F}_{kl}^{(1)}A_{li}}{\varepsilon_i^{(0)}-\varepsilon_k^{(0)}} + A_{kl}A_{il}\right\} = \sum_{l}^{\text{occ}}{}' \left\{\frac{\mathfrak{F}_{kl}^{(1)}}{(\varepsilon_i^{(0)}-\varepsilon_l^{(0)})}\left[\frac{F_{li}^{(1)}-S_{li}^{(1)}\varepsilon_i^{(0)}}{(\varepsilon_i^{(0)}-\varepsilon_k^{(0)})} - \frac{F_{il}^{(1)}-S_{il}^{(1)}\varepsilon_l^{(0)}}{(\varepsilon_l^{(0)}-\varepsilon_k^{(0)})}\right]\right\}\\ + (l=i)\text{ terms}\,.\end{aligned} \tag{41A}$$

The $l=i$ term has to be treated separately, as may be seen from Eq. (18A). Collecting terms in (41A)

$$= -\sum_{l}^{\text{occ}}{}' \frac{A_{kl}\mathfrak{F}_{li}^{(1)}}{(\varepsilon_i^{(0)}-\varepsilon_k^{(0)})} - \sum_{l}^{\text{occ}}{}' \frac{\mathfrak{F}_{kl}^{(1)}S_{il}^{(1)}}{(\varepsilon_l^{(0)}-\varepsilon_k^{(0)})} + (l=i)\text{ terms}\,. \tag{42A}$$

Explicitly including the $l=i$ term, and completing the summation in Eq. (42A) yields

$$\begin{aligned}= -\sum_{l}^{\text{occ}} \frac{A_{kl}\mathfrak{F}_{li}^{(1)}}{(\varepsilon_i^{(0)}-\varepsilon_k^{(0)})} - \sum_{l}^{\text{occ}} \frac{\mathfrak{F}_{kl}^{(1)}S_{il}^{(1)}}{(\varepsilon_l^{(0)}-\varepsilon_k^{(0)})} + \frac{A_{ki}\mathfrak{F}_{ii}^{(1)}}{(\varepsilon_i^{(0)}-\varepsilon_k^{(0)})} + \frac{\mathfrak{F}_{ki}^{(1)}S_{ii}^{(1)}}{(\varepsilon_i^{(0)}-\varepsilon_k^{(0)})}\\ - \tfrac{1}{2}\frac{\mathfrak{F}_{ki}^{(1)}S_{ii}^{(1)}}{(\varepsilon_i^{(0)}-\varepsilon_k^{(0)})} - \tfrac{1}{2}\frac{\mathfrak{F}_{ki}^{(1)}S_{ii}^{(1)}}{(\varepsilon_i^{(0)}-\varepsilon_k^{(0)})}\,.\end{aligned} \tag{43A}$$

Noting that

$$\varepsilon_{ii}^{(1)} = \mathfrak{F}_{ii}^{(1)}, \tag{44A}$$

the third term in (43A) cancels the third term in (40A). Finally, the fourth term is cancelled by the fifth and sixth terms. Thus, collecting terms, Eq. (40A) equals

$$\begin{aligned} 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} g_{ik} \Bigg[\frac{\mathfrak{F}_{ki}^{(2)}}{\varepsilon_i^{(0)} - \varepsilon_k^{(0)}} - \left(\sum_{l}^{\text{occ}} A_{kl} \mathfrak{F}_{li}^{(1)} + \sum_{l}^{\text{all}} S_{kl}^{(1)} \mathfrak{F}_{li}^{(1)} - \sum_{l}^{\text{vac}} \mathfrak{F}_{kl}^{(1)} A_{li} \right) \Big/ (\varepsilon_i^{(0)} - \varepsilon_k^{(0)}) \\ - \sum_{l}^{\text{occ}} A_{kl} S_{il}^{(1)} \Bigg]. \end{aligned} \tag{45A}$$

All of the terms in this equation are non-singular. Thus, the second order change in the density matrix can be written in the following non-singular form which can be applied to problems where the zero order basis contains degenerate orbitals

$$P_{\mu\nu}^{(2)} = 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} \sum_{l}^{\text{vac}} A_{ki} A_{li} C_{\mu k}^{(0)} C_{\nu l}^{(0)} + 2 \sum_{i}^{\text{occ}} \sum_{k}^{\text{all}} g_{ik} \mathfrak{B}_{ki} \tag{46A}$$

where, if both *i* and *k* are occupied

$$\mathfrak{B}_{ki} = -\tfrac{1}{2} \left[\sum_{l}^{\text{vac}} A_{il} A_{kl} - \sum_{l}^{\text{all}} S_{il}^{(1)} S_{lk}^{(1)} + S_{ki}^{(2)} \right] \tag{47A}$$

and if *i* occupied and *k* vacant

$$\begin{aligned} \mathfrak{B}_{ki} = \mathfrak{F}_{ki}^{(2)} / (\varepsilon_i^{(0)} - \varepsilon_k^{(0)}) - \left(\sum_{l}^{\text{occ}} A_{kl} \mathfrak{F}_{li}^{(1)} + \sum_{l}^{\text{all}} S_{kl}^{(1)} \mathfrak{F}_{li}^{(1)} - \sum_{l}^{\text{vac}} \mathfrak{F}_{kl}^{(1)} A_{li} \right) \Big/ (\varepsilon_i^{(0)} - \varepsilon_k^{(0)}) \\ - \sum_{l}^{\text{occ}} A_{kl} S_{il}^{(1)}. \end{aligned} \tag{48A}$$

The calculation of $P^{(2)}$ must also be iterative because of the presence of $\mathfrak{F}^{(2)}$ in Eq. (48A). However, it should be noted that the most complicated terms required for the evaluation of $P^{(2)}$ need be calculated only once, prior to the start of the iterative calculation. In fact, the non-iterative contribution to $P^{(2)}$ may be used as a first guess to initiate the second order calculation.

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