

Off-diagonal long-range order of the wave function in terms of the alternate molecular bonding geminals

LÜ, Wen-Cai* (吕文彩) SUN, Chia-Chung (孙家钟)

State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun, Jilin 130023, China

It is shown that in the quantum structural approach to high- T_c superconductivity, the wave function in terms of the alternate molecular bonding geminals possesses off-diagonal long-range order (ODLRO).

Keywords Alternate molecular bonding geminals, quantum structural approach, off-diagonal long-range order

Introduction

Recently, Chiu proposed a quantum structural ap-

proach to high- T_c superconductivity,^{1,2} in which some possible thoughts of quantum chemical structures are compared and mixed with the physical treatments of high- T_c superconductors. In the approach the molecular bonding geminal (MBG) ψ_Λ is expressed as Bloch sum of the bonding geminals (BG) $\varphi_{n,n+1}$ such that¹

$$\psi_\Lambda(1,2) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{i2\pi\Lambda n/N} \varphi_{n,n+1}(1,2) \quad (1)$$

$$\varphi_{n,n+1}(1,2) = \frac{1}{\sqrt{2}} [\varphi_n(x_1)\varphi_{n+1}(x_2) + \varphi_n(x_2)\varphi_{n+1}(x_1)] \times \frac{1}{\sqrt{2}} [\alpha_1\beta_2 - \beta_1\alpha_2] \quad (2)$$

where

In Eq. (2), 1 and 2 on the left side stand for the spin-orbital coordinates of the first and second particles, x_1 and x_2 for their orbital coordinates, and α and β for spin up and spin down, respectively. The vibrational pseudo-

angular momentum Λ can take the values of $0, \pm 1, \dots, \pm (\frac{N}{2} - 1), \frac{N}{2}$ (for even N). In terms of ψ_Λ in Eq. (1), the vibronic geminal is given by

$$\psi(1,2) = \psi_0(1,2) + \sum_{\Lambda} \frac{\langle \psi_\Lambda(1,2) \chi^1(Q_{-\Lambda}) \left| \frac{\partial H}{\partial Q_{-\Lambda}} Q_{-\Lambda} \right| \psi_0(1,2) \chi^0(Q_{-\Lambda}) \rangle}{E_0 - E_\Lambda - E_{-\Lambda}^Q} \times \psi_\Lambda(1,2) \chi^1(Q_{-\Lambda}) \quad (3)$$

where χ^0 and χ^1 represent respectively zero and one vibrational quantum number of the eigenfunctions, and the vibrational mode Q_Λ is taken to be the linear combination of $q_{n,n+1} = \zeta_{n+1} - \zeta_n$ (ζ_n is the local atom n 's

movement), similar to the linear combination of bonding geminals in Eq. (1). By means of the vibronic geminal the completely antisymmetrized wave function of M electron/hole pairs is written as

* Received August 23, 1999; accepted December 17, 1999.

Project (No. 29892168) supported by the National Natural Science Foundation of China.

$$\Psi(123\cdots 2M) = A_{2M}\psi(1,2)\psi(3,4)\cdots\psi(2M-1,2M) \quad (4)$$

where A_{2M} is the normalized antisymmetrizer. As a special and important case, the wave function for the half-filled system with $M = N/2$ electron/hole pairs was considered.^{1,2} It is noted that in the quantum structural

approach electrons/holes are described by geminals, and the Jahn-Teller and Renner-Teller perturbations³⁻⁵ for degenerate states ψ_{Λ} and $\psi_{-\Lambda}$ based on the Herzberg-Teller expansion are much more emphasized.

$$H = H_0 + \sum_q \frac{\partial H}{\partial Q_q} Q_q + \frac{1}{2!} \sum_q \sum_{q'} \frac{\partial^2 H}{\partial Q_q \partial Q_{q'}} Q_q Q_{q'} + \cdots \quad (5)$$

In the application of the quantum structural approach to high- T_c superconductivity, the important case of alternating double O^- holes $\cdots \boxed{=}\boxed{=}\boxed{=}\cdots$, with $\boxed{=}$ standing for quadruple unit composed of CuO_2 cells, was considered to be comparable with that of the conjugate carbon chain with alternating conjugate π -electron

bonding $\cdots C=C-C=C-C \cdots$ (for the detailed comparison, see Ref. 1). As a simplest illustration, the C_4H_4 case $C(0)-C(1)-C(2)-C(3)-C(4)$ with cyclic boundary condition $C(4) = C(0)$ was discussed. The corresponding alternate MBGs (ψ_1^x and ψ_1^y) were expressed as¹

$$\psi_1^x(1,2) = \frac{1}{\sqrt{2}}[\psi_1(1,2) + \psi_{-1}(1,2)] = \frac{1}{\sqrt{2}}[\varphi_{0,1}(1,2) - \varphi_{2,3}(1,2)] \quad (6)$$

$$\psi_1^y(1,2) = \frac{1}{i\sqrt{2}}[\psi_1(1,2) - \psi_{-1}(1,2)] = \frac{1}{\sqrt{2}}[\varphi_{1,2}(1,2) - \varphi_{3,0}(1,2)] \quad (7)$$

It has been shown that the antisymmetric vibration $\pm Q_2$ would be in energy lower one of ψ_1^x , ψ_1^y and raise the other simultaneously. $+Q_2$, the positive vibration ($\leftarrow C C \rightarrow \leftarrow C C \rightarrow \leftarrow C$), favors and lowers the bond energy of $C-C=C-C=C$, while $-Q_2$, the negative vibration ($C \rightarrow \leftarrow C C \rightarrow \leftarrow C C \rightarrow$), favors and lowers the bond energy of $C=C-C=C-C$. This can result in a double-well potential with two resonant minima and a potential barrier between them, which is similar to the Jahn-Teller effect.³⁻⁵ As is suggested,¹ the double-well potential barrier may relate to the energy gap for the superconducting double-electron pairs $C=C-C=C-C$ which can be raised and disinte-

grated into $C-C-C-C-C$. In the 1976 paper of Chiu and Wang,⁶ the similar barrier for pair-wise charge transfer from $C=C-C$ to $C-C=C$ was estimated to be $E_c = 0.20 \times 10^{-13} \text{ erg} \approx 145^\circ k$, which seems to be comparable to the current high- T_c number.

However, we may inquire whether the alternate MBG can really exhibit the superconducting behavior. For this purpose, an attempt is made in this paper to demonstrate the superconducting property of the general alternate MBGs $\psi_{N/4}^x$ and $\psi_{N/4}^y$ (with $\Lambda = N/4$ for $N = 4N'$ units, N' is integer), which, generalized from ψ_1^x and ψ_1^y , can be written as

$$\psi_{N/4}^x(1,2) = \frac{1}{\sqrt{2}}[\psi_{N/4}(1,2) + \psi_{-N/4}(1,2)] = \sqrt{\frac{2}{N}} \sum_{n=0}^{\frac{N}{2}-1} \xi_{2n} \varphi_{2n,2n+1}(1,2) \quad (8)$$

$$\psi_{N/4}^y(1,2) = \frac{1}{i\sqrt{2}}[\psi_{N/4}(1,2) - \psi_{-N/4}(1,2)] = \sqrt{\frac{2}{N}} \sum_{n=0}^{\frac{N}{2}-1} \xi_{2n+1} \varphi_{2n+1,2n+2}(1,2) \quad (9)$$

where

$$\xi_{2n} = \xi_{2n+1} = (-1)^n \quad (10)$$

As is well known, Yang showed that the off-diagonal long-range order (ODLRO) is an essential characteristic

$$\Psi_{N/4}^x(123\cdots 2M) = A_{2M} \psi_{N/4}^x(1,2) \psi_{N/4}^x(3,4) \cdots \psi_{N/4}^x(2M-1,2M) \quad (11)$$

and

$$\Psi_{N/4}^y(123\cdots 2M) = A_{2M} \psi_{N/4}^y(1,2) \psi_{N/4}^y(3,4) \cdots \psi_{N/4}^y(2M-1,2M) \quad (12)$$

In Sec. II it is shown that the second-order reduced density matrices of $\Psi_{N/4}^x$ and $\Psi_{N/4}^y$ possess the largest eigenvalue for a system which has $2N$ states with $2M$ fermions, indicating that $\Psi_{N/4}^x$ and $\Psi_{N/4}^y$ possess ODLRO.⁷ In Sec. III we make further discussions on the wave functions Ψ' in Eq. (32) and Ψ'' in Eq. (36) in order to reveal the corresponding damages to the largest eigenvalue.

ODLRO of $\Psi_{N/4}^x$ and $\Psi_{N/4}^y$ with respect to the alternate MBGs

At first it is noticed that the alternate MBGs of spin singlet are different from the Cooper-pairing⁸

$$\eta_c = \sum_r a_r b_r \quad (13)$$

and the on-site as well as the extended η pairings of Yang,⁹

$$\eta = \sum_r e^{-i\pi \cdot r} a_r b_r \quad (14)$$

$$\eta_a = \sum_r e^{-i\pi \cdot r} a_{r+a} b_r \quad (15)$$

where a_r and b_r are coordinate-space annihilation operators for spin-up and spin-down electrons/holes, respectively, and the subscripts $r+a$ and r in Eq. (15) denote an extended pairing at a distance of a . The differences are made clear when the alternate MBGs are written in the second quantization formalisms

of superconductivity.⁷ Therefore we will investigate the property of the second-order reduced density matrices of the completely antisymmetrized wave functions $\Psi_{N/4}^x$ and $\Psi_{N/4}^y$ with respect to $\psi_{N/4}^x$ and $\psi_{N/4}^y$, given by

$$\begin{aligned} \psi_{N/4}^x &= \sum_r \cos\left(\frac{\pi}{2} r\right) (a_r b_{r+1} - b_r a_{r+1}) \\ \psi_{N/4}^y &= \sum_r \sin\left(\frac{\pi}{2} r\right) (a_r b_{r+1} - b_r a_{r+1}) \end{aligned} \quad (16)$$

where r stands for n .

Now let us consider the wave function $\Psi_{N/4}^x$ ($\Psi_{N/4}^y$ can be discussed similarly). In the following, let $\varphi_{n\alpha}$ and $\varphi_{n\beta}$ represent $\varphi_{n\alpha}$ and $\varphi_{n\beta}$, γ_l with $l = 1, 2$ stand for α and β , respectively. Then it is obvious from Eq. (2) that the bonding geminal $\varphi_{n,n+1}$ of spin singlet can be written in the form

$$\varphi_{n,n+1}(1,2) = \frac{1}{\sqrt{2}} [\varphi_{n,n+1}^{(1)}(1,2) - \varphi_{n,n+1}^{(2)}(1,2)] \quad (17)$$

where

$$\begin{aligned} &\varphi_{n,n+1}^{(1)}(1,2) \\ &= \frac{1}{\sqrt{2}} [\varphi_{n\alpha}(1) \varphi_{(n+1)\beta}(2) - \varphi_{n\alpha}(2) \varphi_{(n+1)\beta}(1)] \end{aligned} \quad (18)$$

$$\begin{aligned} &\varphi_{n,n+1}^{(2)}(1,2) \\ &= \frac{1}{\sqrt{2}} [\varphi_{n\beta}(1) \varphi_{(n+1)\alpha}(2) - \varphi_{n\beta}(2) \varphi_{(n+1)\alpha}(1)] \end{aligned} \quad (19)$$

Thus the alternate MBGs $\Psi_{N/4}^x$ and $\Psi_{N/4}^y$ in Eqs. (8) and (9) can be rewritten as

$$\psi_{N/4}^x(1,2) = \sqrt{\frac{1}{N}} \sum_{n=0}^{\frac{N}{2}-1} \xi_{2n} [\varphi_{2n,2n+1}^{(1)}(1,2) - \varphi_{2n,2n+1}^{(2)}(1,2)] \quad (20)$$

and

$$\psi_{N/4}^y(1,2) = \sqrt{\frac{1}{N}} \sum_{n=0}^{\frac{N}{2}-1} \xi_{2n+1} [\varphi_{2n+1,2n+2}^{(1)}(1,2) - \varphi_{2n+1,2n+2}^{(2)}(1,2)] \quad (21)$$

Substituting Eq. (20) to Eq. (11) the antisymmetrized Slater determinants such that wave function $\Psi_{N/4}^x$ can be expanded by the normalized

$$\Psi_{N/4}^x(123 \cdots 2M) = \left[\frac{N!}{M!(N-M)!} \right]^{-\frac{1}{2}} \sum_{I,K} \Psi_{I,K}^x(123 \cdots 2M) \quad (22)$$

where

$$\Psi_{I,K}^x(123 \cdots 2M) = \left[\prod_{m=1,2,\dots,M} \xi_{2i_m} (-1)^{k_m+1} \right] [\varphi_{2i_1,2i_1+1}^{(k_1)} \varphi_{2i_2,2i_2+1}^{(k_2)} \cdots \varphi_{2i_M,2i_M+1}^{(k_M)}] \quad (23)$$

In Eq. (22), $I = \{(2i_1, 2i_1 + 1), (2i_2, 2i_2 + 1), \dots, (2i_m, 2i_m + 1), \dots, (2i_M, 2i_M + 1)\}$ that denotes a series of M different BG locations, K stands for $\{k_1, k_2, \dots, k_m, \dots, k_M\}$ with $k_m = 1$ or 2 . The normalized Slater determinant $[\varphi_{2i_1,2i_1+1}^{(k_1)} \varphi_{2i_2,2i_2+1}^{(k_2)} \cdots \varphi_{2i_M,2i_M+1}^{(k_M)}]$ in Eq. (23) is defined by

$$[\varphi_{2i_1,2i_1+1}^{(k_1)} \varphi_{2i_2,2i_2+1}^{(k_2)} \cdots \varphi_{2i_M,2i_M+1}^{(k_M)}] = \frac{1}{\sqrt{2^M (2M)!}} \sum_{\nu=1}^{(2M)!} \delta_{\nu} P_{\nu} \{ \varphi_{2i_1,2i_1+1}^{(k_1)}(1,2) \varphi_{2i_2,2i_2+1}^{(k_2)}(3,4) \cdots \varphi_{2i_M,2i_M+1}^{(k_M)}(2M-1,2M) \} \quad (24)$$

where δ_{ν} is the parity factor of the permutation operator P_{ν} . By means of the conventional method the second-order reduced density matrix ρ_2 of $\Psi_{N/4}^x$ can be written in the form

$$\begin{aligned} \rho_2(1,2;1',2') &= 2M(2M-1) \int \Psi_{N/4}^x(123 \cdots 2M) \Psi_{N/4}^{x*}(1'2'3 \cdots 2M) d(3 \cdots 2M) \\ &= \sum_{i \leq j, i' \leq j', i, m, l, m'} \varphi_{i\gamma_i, j\gamma_m}(1,2) \varphi_{i'\gamma_i, j'\gamma_m}^*(1',2') P_{ijm, i'l'j'm'} \end{aligned} \quad (25)$$

where P is the matrix representation of ρ_2 and where

$$\varphi_{i\gamma_i, j\gamma_m}(1,2) = \frac{1}{\sqrt{2}} [\varphi_{i\gamma_i}(1) \varphi_{j\gamma_m}(2) - \varphi_{i\gamma_i}(2) \varphi_{j\gamma_m}(1)] \quad (26)$$

Substituting Eq. (22) into Eq. (25) we can obtain

$$\begin{aligned}
\rho_2(1,2;1',2') &= \sum_{i,k,l,k'} \varphi_{2i,2i+1}^{(k)}(1,2) \varphi_{2i',2i'+1}^{(k')*}(1',2') 2^{M+1} C_{N-2}^{M-1} / (2^M C_N^M) U_{(2i)k,(2i')k'} \\
&+ \sum_{i \leq j,l,m} \varphi_{i\gamma_l, j\gamma_m}(1,2) \varphi_{i\gamma_l, j\gamma_m}^*(1',2') 2^{M+1} C_{N-2}^{M-2} / (2^M C_N^M) E_{ijlm, ijlm} \\
&= \sum_{i,k,l,k'} \varphi_{2i,2i+1}^{(k)}(1,2) \varphi_{2i',2i'+1}^{(k')*}(1',2') \frac{2M(N-M)}{N(N-1)} U_{(2i)k,(2i')k'} \\
&+ \sum_{i \leq j,l,m} \varphi_{i\gamma_l, j\gamma_m}(1,2) \varphi_{i\gamma_l, j\gamma_m}^*(1',2') \frac{2M(M-1)}{N(N-1)} E_{ijlm, ijlm} \quad (27)
\end{aligned}$$

where E is the unit matrix and $U_{(2i)k,(2i')k'}$ takes the form of

$$U_{(2i)k,(2i')k'} = \xi_{2i} \xi_{2i'} (-1)^{k+k'} \quad (28)$$

By comparison of Eq. (27) with Eq. (25) it is easy to give

$$P = \frac{2M(M-1)}{N(N-1)} E + \frac{2M(N-M)}{N(N-1)} \begin{pmatrix} U & 0 \\ 0 & 0 \end{pmatrix} \quad (29)$$

where the matrix elements of U is defined by Eq. (28). Now it can be easily seen from Eq. (28) that the alternate MBG $\psi_{N/4}^x$ in Eq. (20) is the eigenfunction of U with the eigenvalue of N . As a direct result of Eqs. (25) and (29), the alternate MBG $\psi_{N/4}^x$ is shown to be the eigenfunction of ρ_2 , i. e.,

$$\begin{aligned}
\int \rho_2(1,2;1',2') \psi_{N/4}^x(1',2') d1' d2' \\
= \lambda_2 \psi_{N/4}^x(1,2) \quad (30)
\end{aligned}$$

where

$$\begin{aligned}
\lambda_2 &= \frac{2M(M-1)}{N(N-1)} + \frac{2M(N-M)}{N(N-1)} N \\
&= 2M(N-M+1)/N \quad (31)
\end{aligned}$$

At this point we notice that λ_2 is just the largest eigenvalue of ρ_2 for a system which possesses $2N$ states with $2M$ fermions, given by Yang.⁷ In the case of the half-filled ($M = N/2$) system, λ_2 reaches to $N/2 + 1$. Moreover, it can be shown similarly that the alternate MBG $\psi_{N/4}^y$ in Eq. (9) is the eigenfunction of the corresponding second-order reduced density matrix of the wave function $\Psi_{N/4}^y$ in Eq. (12), with the same largest

eigenvalue λ_2 .

As is known, the wave function with the largest eigenvalue of the second-order reduced density matrix does have ODLRO.⁷ Thus it is shown that $\Psi_{N/4}^x$ and $\Psi_{N/4}^y$ with respect to $\psi_{N/4}^x$ and $\psi_{N/4}^y$ have ODLRO, indicating that the alternate MBGs $\psi_{N/4}^x$ and $\psi_{N/4}^y$ as shown in Fig. 1 possess the superconducting property.

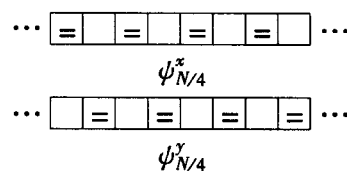


Fig. 1 Illustration of the alternate MBGs $\psi_{N/4}^x$ and $\psi_{N/4}^y$.

Discussion on the breakage to the largest eigenvalue of ρ_2

As noted, the resonant alternate MBGs $\psi_{N/4}^x$ and $\psi_{N/4}^y$ can transit to each other *via* the antisymmetric vibration.¹ The result is a double-well potential, which is considered to be related to the superconducting gap.^{1,2} Here we notice that there exists a transition condition: when the electrons appear in the state $\psi_{N/4}^x$, the state $\psi_{N/4}^y$ could not be occupied. Otherwise the corresponding transition would be banned; and the largest eigenvalue of ρ_2 as well as the double-well potential would be damaged to some extent. Now consider the simplest case of such damage with the wave function

$$\begin{aligned}
\Psi'(123 \cdots 2M) &= A_{2M} \psi_{N/4}^x(1,2) \psi_{N/4}^y(3,4) \cdots \\
&\psi_{N/4}^x(2M-3, 2M-2) \psi_{N/4}^y(2M-1, 2M) \quad (32)
\end{aligned}$$

which is supposed to contain a different pair of $\psi_{N/4}^x$. In this case the second-order reduced density matrix ρ_2' for Ψ' is defined by

$$\rho_2'(1,2;1',2') = 2M(2M-1) \int \Psi'(123\cdots 2M) \Psi'^*(1'2'3\cdots 2M) d(3\cdots 2M) \quad (33)$$

Similar to the demonstration of Eq. (30), the alternate MBG $\psi_{N/4}^x$ can be shown (see appendix) to be the eigenfunction of ρ_2' with a larger, but not the largest, eigenvalue λ_2' , *i. e.*,

$$\int \rho_2'(1,2;1',2') \psi_{N/4}^x(1',2') d1' d2' = \lambda_2' \psi_{N/4}^x(1,2) \quad (34)$$

where

$$\lambda_2' = \frac{2(M-1)(N-M-1)}{N} + \frac{2(M-1)}{N} = \lambda_2 - 2 \quad (35)$$

Here λ_2 is the largest eigenvalue given by Eq. (31).

Then we can discuss similarly the wave function with a different electron/hole pair of spin triplet,

$$\Psi''(123\cdots 2M) = A_{2M} \psi_{N/4}^x(1,2) \psi_{N/4}^x(3,4) \cdots \psi_{N/4}^x(2M-3,2M-2)^3 \psi_{N/4}^x(2M-1,2M) \quad (36)$$

where

$${}^3\psi_{N/4}^x(1,2) = \sqrt{\frac{2}{N}} \sum_{n=0}^{\frac{N}{2}-1} \xi_{2n} {}^3\varphi_{2n,2n+1}(1,2) \quad (37)$$

with

$${}^3\varphi_{n,n+1}(1,2) = \frac{1}{\sqrt{2}} [\varphi_{n,n+1}^{(1)}(1,2) + \varphi_{n,n+1}^{(2)}(1,2)] \quad (38)$$

Notice that $\varphi_{n,n+1}^{(1)}$ and $\varphi_{n,n+1}^{(2)}$ are defined by Eqs. (18) and (19), respectively. For Ψ'' , the second-or-

der reduced density matrix ρ_2'' is expressed as

$$\rho_2''(1,2;1',2') = 2M(2M-1) \int \Psi''(123\cdots 2M) \Psi''^*(1'2'3\cdots 2M) d(3\cdots 2M) \quad (39)$$

It can be shown easily (see appendix) that the alternate

MBG $\psi_{N/4}^x$ is now the eigenfunction of ρ_2'' with

$$\int \rho_2''(1,2;1',2') \psi_{N/4}^x(1',2') d1' d2' = \lambda_2'' \psi_{N/4}^x(1,2) \quad (40)$$

where

$$\lambda_2'' = \lambda_2' = \lambda_2 - 2 \quad (41)$$

As expected, due to the existence of a different pair of $\psi_{N/4}^x$ or ${}^3\psi_{N/4}^x$, the larger eigenvalues λ_2' , λ_2'' with re-

spect to ρ_2' , ρ_2'' are lowered by 2 against the largest eigenvalue λ_2 .

Appendix

For Ψ' defined by Eq. (32), the second-order reduced density matrix ρ_2' can be expanded as follows

$$\begin{aligned} \rho_2'(1, 2; 1', 2') &= 2M(2M-1) \int \Psi'(123\cdots 2M) \Psi'^*(1'2'3\cdots 2M) d(3\cdots 2M) \\ &= \sum_{i,k,i',k'} \varphi_{2i,2i+1}^{(k)}(1, 2) \varphi_{2i',2i'+1}^{(k)*}(1', 2') P'_{(2i)k,(2i')k'} \\ &\quad + \sum_{i,k,i',k'} \varphi_{2i+1,2i+2}^{(k)}(1, 2) \varphi_{2i'+1,2i'+2}^{(k)*}(1', 2') P'_{(2i+1)k,(2i'+1)k'} \\ &\quad + \sum_{\substack{i \leq j, i' \leq j', i, m, i' = i, i \pm 2; j = j, j \pm 2 \\ (j, m) \neq (i+1, i \pm 1), (j', m) \neq (i'+1, i' \pm 1)}} \varphi_{i\gamma_1, j\gamma_m}(1, 2) \varphi_{i'\gamma_1, j'\gamma_m}^*(1', 2') P'_{ijm, i'lj'm} \quad (\text{A.1}) \end{aligned}$$

To facilitate our discussion we define a 2×2 coefficient matrix $P'_{2i,2i}$ by

$$P'_{2i,2i'} = [(P'_{(2i)k,(2i')k'})] = \begin{pmatrix} P'_{(2i)1,(2i')1} & P'_{(2i)1,(2i')2} \\ P'_{(2i)2,(2i')1} & P'_{(2i)2,(2i')2} \end{pmatrix} \quad (\text{A.2})$$

Substituting Eq. (32) into Eq. (A.1) we can obtain

$$P'_{2i,2i} = \frac{2}{NC_{N-2}^{M-1}} \begin{pmatrix} (N-2)C_{N-3}^{M-2} & -(N-4)C_{N-4}^{M-2} \\ -(N-4)C_{N-4}^{M-2} & (N-2)C_{N-3}^{M-2} \end{pmatrix} \quad (\text{A.3})$$

$$P'_{2i,2(i+1)} = P'_{2i,2(i-1)} = -\frac{2C_{N-4}^{M-2}}{NC_{N-2}^{M-1}} \begin{pmatrix} (N-3) & -(N-4) \\ -(N-4) & (N-3) \end{pmatrix} \quad (\text{A.4})$$

and for $i' \neq i, i \pm 1$,

$$P'_{2i,2i'} = (-1)^{i+i'} \frac{2(N-4)C_{N-4}^{M-2}}{NC_{N-2}^{M-1}} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad (\text{A.5})$$

Making use of the above expressions for $P'_{2i,2i'}$ and the cyclic boundary condition of crystals, we can easily show that

$$\begin{aligned} &\int \rho_2'(1, 2; 1', 2') \psi_{N/4}^x(1', 2') d1' d2' \\ &= \int \sum_{i,k,i',k'} \varphi_{2i,2i+1}^{(k)}(1, 2) \varphi_{2i',2i'+1}^{(k)*}(1', 2') P'_{(2i)k,(2i')k'} \psi_{N/4}^x(1', 2') d1' d2' = \lambda_2' \psi_{N/4}^x(1, 2) \quad (\text{A.6}) \end{aligned}$$

where

$$\begin{aligned} \lambda_2' &= \frac{2}{NC_{N-2}^{M-1}} [(N-2)C_{N-3}^{M-2} + 2(N-3)C_{N-4}^{M-2} + (N-3)(N-4)C_{N-4}^{M-2}] \\ &= \frac{2(M-1)(N-M-1)}{N} + \frac{2(M-1)}{N} = \lambda_2 - 2 \quad (\text{A.7}) \end{aligned}$$

where λ_2 is the largest eigenvalue given by Eq. (31). For Ψ'' given by Eq. (36), the second-order reduced density matrix ρ_2'' can be expressed as

$$\begin{aligned} \rho_2''(1,2;1',2') &= 2M(2M-1) \int \Psi''(123\cdots 2M) \Psi''^*(1'2'3\cdots 2M) d(3\cdots 2M) \\ &= \sum_{i,k,l,k'} \varphi_{2i,2i+1}^{(k)}(1,2) \varphi_{2i',2i'+1}^{(k')*}(1',2') P''_{(2i)k,(2i')k'} \\ &\quad + \sum_{\substack{i \leq j,l,m \\ (j,m) \neq (i+1,l \pm 1)}} \varphi_{i',j'}(1,2) \varphi_{i',j'}^*(1',2') P''_{ijm,ijm} \end{aligned} \quad (\text{A.8})$$

Defined similarly as $P'_{2i,2i'}$ by Eq. (A.2), the 2×2 coefficient matrix $P''_{2i,2i'}$ with the matrix elements $P''_{(2i)k,(2i')k'}$ can be obtained as

$$P''_{2i,2i} = \frac{2(N-2)}{NC_{N-2}^{M-1}} \begin{pmatrix} C_{N-3}^{M-2} & -C_{N-4}^{M-2} \\ -C_{N-4}^{M-2} & C_{N-3}^{M-2} \end{pmatrix} + \frac{2}{N} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (\text{A.9})$$

and for $i' \neq i$,

$$P''_{2i,2i'} = (-1)^{i+i'} \frac{2(N-4)C_{N-4}^{M-2}}{NC_{N-2}^{M-1}} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} + (-1)^{i+i'} \frac{2C_{N-4}^{M-1}}{NC_{N-2}^{M-1}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (\text{A.10})$$

Using Eqs. (A.9) and (A.10) it is easy to prove

$$\begin{aligned} \int \rho_2''(1,2;1',2') \psi_{N/4}^x(1',2') d1' d2' &= \int \sum_{i,k,l,k'} \varphi_{2i,2i+1}^{(k)}(1,2) \varphi_{2i',2i'+1}^{(k')*}(1',2') P''_{(2i)k,(2i')k'} \psi_{N/4}^x(1',2') d1' d2' \\ &= \lambda_2'' \psi_{N/4}^x(1,2) \end{aligned} \quad (\text{A.11})$$

where

$$\begin{aligned} \lambda_2'' &= \frac{2}{NC_{N-2}^{M-1}} [(N-2)C_{N-3}^{M-2} + (N-2)(N-3)C_{N-4}^{M-2}] \\ &= \frac{2(M-1)(N-M-1)}{N} + \frac{2(M-1)}{N} = \lambda_2 - 2 \end{aligned} \quad (\text{A.12})$$

References

1. Chiu, Y.N., *Theor. Chim. Acta*, **90**, 205(1995).
2. Chiu, Y.N., *Phys. Rev. B*, **55**, 6022(1997).
3. a) Bersuker, I.B., *The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum, New York, 1984.
b) Chiu, Y.N., *Phys. Rev. A*, **32**, 2257(1985).
4. Herzberg, G., *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand, Princeton, New Jersey, 1966.
5. a) Chiu, Y.N., *J. Chem. Phys.*, **64**, 2997(1976).
b) Chiu, Y.N.; Friedrich, B.; Maring, W.; Niedner, G.; Noll, M.; Toennies, J.P., *J. Chem. Phys.*, **88**, 6814(1988).
c) Chiu, Y.N., *J. Phys. Chem.*, **88**, 5820(1984).
6. a) Wang, F.E.; Chiu, Y.N., *Chem. Phys.*, **12**, 225(1976).
b) Chiu, Y.N.; Wang, F.E., *Chem. Phys.*, **18**, 301(1976).
7. Yang, C.N., *Rev. Mod. Phys.*, **34**, 694(1962).
8. Cooper, L.N., *Phys. Rev.*, **104**, 1189(1956).
9. Yang, C.N., *Phys. Rev. Lett.*, **63**, 2144(1989).