Structural and vibrational properties of fullerenes and nanotubes in a nonorthogonal tight-binding scheme

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A simple, computationally efficient method for the evaluation of structural and vibrational properties of carbon is presented. The scheme is based on the generalized tight-binding molecular dynamics technique applicable to covalent systems. The force constants for the evaluation of vibrational modes are obtained by employing analytic second derivatives of the electronic structure Hamiltonian matrix elements. This method, while providing better accuracy than conventional schemes, greatly expedites the determination of vibrational modes for large size clusters. The efficacy of the method is demonstrated by application to fullerenes and nanotubes. Good agreement is obtained with experiment for bond lengths and vibrational frequencies for these systems.

I. INTRODUCTION

The interest in pure carbon systems was rekindled by the discovery of highly stable caged forms of carbon. Among the group IV elements carbon is unique in that its special chemistry allows it to form stable clusters with widely differing coordination in the form of chains, rings, and fullerenes.

Theoretical studies, ranging from ab initio, semiempirical, to classical potential methods have been reported in different size ranges. Recently, we introduced a generalized tight-binding molecular dynamics (GTBMD) scheme that allows for full relaxation of covalent systems with no symmetry constraints. This method is orders of magnitude faster than local density approximation (LDA) or ab initio schemes and has been applied to obtain equilibrium geometries for small silicon and carbon clusters in good agreement with ab initio results.

Our method has been used to predict a new structure for Si12 cluster. Of particular interest are the dynamical properties of carbon clusters. Advances in experimental techniques have made it possible to readily determine the vibrational spectrum of clusters. The ab initio methods, while accurately describing the vibrational properties of small clusters and molecules, are impractical for the treatment of intermediate or large systems, except in cases where a high degree of symmetry exists (e.g., C60). The effects on the vibrational properties due to such symmetry lowering effects as doping, polymerization, or chemisorption, however, make detailed ab initio studies of quantities of interest to experimentalists prohibitively expensive. It is, therefore, desirable to have a simple and computationally efficient scheme that can be used for full symmetry unrestricted relaxation, as well as for the determination of the vibrational spectrum in a consistent manner for clusters of arbitrary sizes.

In this paper we present modifications and extensions of the GTBMD scheme that vastly improve the speed and accuracy of the frequency determination for large clusters. Specifically, analytic second derivatives for the evaluation of force constants are incorporated. This allows us to circumvent the computationally inefficient procedure of evaluating force constants by computing energy changes due to mutual displacements used commonly in ab initio and other semiempirical schemes. Furthermore, the present scheme is also orders of magnitude faster than numerically differentiating the forces obtained by the Hellmann–Feynman theorem for the construction of the dynamical matrix, traditionally used in semiempirical molecular dynamics methods.

The details of the GTBMD scheme as applied to silicon systems are given in Refs. 2–4. In Sec. II we give a brief overview and give details on the construction of the dynamical matrix for obtaining vibrational modes. Results are presented in Sec. III, and a summary is given in Sec. IV.

II. TECHNIQUE

The total energy of the system is given by the sum

\[ U = U_{el} + U_{rep} , \]

where \( U_{el} \) is the sum of the one-electron energies \( e_k \) for the occupied states,

\[ U_{el} = \sum_k E_k , \]

and \( U_{rep} \) is given by a repulsive pair potential

\[ U_{rep} = \sum_i \sum_{j>i} \phi(r_{ij}) . \]

Here \( r_{ij} \) is the separation of atoms \( i \) and \( j \). As in our earlier work, \( \phi(r) \) is short ranged and taken to scale exponentially with distance. To fix absolute energies either a constant or a coordination dependent energy term is added to Eq. (1). However, our interest here is in the vibrational properties, for which such a term is irrelevant.

In the nonorthogonal tight-binding scheme the characteristic equation is written, in matrix form, as

\[ (H - E_n S)C_n = 0 , \]

where \( S \) is the overlap matrix of the nonorthogonal basis set. In the GTBMD scheme the dynamical matrix is written as

\[ S = \sum_n C_n C_n^T , \]

and

\[ H = \sum_n C_n C_n^T \frac{1}{2} \frac{\partial^2 E}{\partial C_n \partial C_n^T} \frac{1}{2} \frac{\partial^2 E}{\partial C_n \partial C_n^T} . \]
where $\mathbf{C}^n$ is a column vector of LCAO coefficients, $\mathbf{H}$ is the Hamiltonian matrix, and $\mathbf{S}$ the overlap matrix of the LCAO basis set.

The Hellmann–Feynman theorem for obtaining the electronic part of the force is given by

$$\frac{\partial E_n}{\partial \mathbf{r}} = \mathbf{C}^n \left[ \frac{\partial \mathbf{H}}{\partial \mathbf{r}} - E_n \frac{\partial \mathbf{S}}{\partial \mathbf{r}} \right] \mathbf{C}^\dagger \mathbf{C}^n.$$

(5)

The $\mathbf{C}^n$ are normalized so that

$$\mathbf{C}^\dagger \mathbf{C} = \mathbf{I}.$$

(6)

In the conventional, solid state approach, which we call the "orthogonal" approach, the basis set is presumed to be an orthogonal set ($S_{ij} = \delta_{ij}$). In the Slater–Koster scheme the Hamiltonian matrix elements are obtained from the parameters $V_{\lambda\lambda',\mu}$ in terms of the bond direction cosines $l, m, n$.$^{17,18}$

$$
\begin{align*}
V_{\lambda\lambda'}(r) &= V_{ss\sigma}(r), \\
V_{\lambda m}(r) &= lV_{sp\sigma}(r), \\
V_{\lambda n}(r) &= l^2 V_{pp\sigma}(r) + (1 - l^2) V_{pp\sigma}(r), \\
V_{\lambda s}(r) &= l m V_{pp\sigma}(r) - l m V_{pp\sigma}(r).
\end{align*}
$$

(7)

In Table I we list the parameters $V_{\lambda\lambda',\mu}$ used in the present work for carbon. The $V_{\lambda\lambda',\mu}(r)$ are taken to decrease exponentially with $r$:

$$V_{\lambda\lambda',\mu}(r) = V_{\lambda\lambda'}(d_0) e^{-\alpha(r-d_0)},$$

(8)

where $d_0$ is the sum of the covalent radii of the pair of interacting atoms and $\alpha$ is an adjustable parameter. The scaling of the repulsive term is also taken to be exponential,

$$\phi(r) = \phi_0 e^{-\beta(r-d_0)},$$

(9)

where we choose $\beta=4\alpha$.$^2$

This method was extended by van Schilfgaarde and Harrison within the context of total energy calculation in the presence of nonorthogonality.$^{19}$ They calculated the overlap matrix in the spirit of extended Hückel theory$^{20}$ by assuming a proportionality between $\mathbf{H}$ and $\mathbf{S}$:

$$S_{ij} = \frac{2}{K} \frac{H_{ij}}{H_{ii} + H_{jj}}.$$

(10)

The diagonal elements of $H_{ij}$, as in the orthogonal theory, are taken to be the valence $s$ and $p$ energies. The off-diagonal interatomic matrix elements are given in terms of the Hamiltonian matrix elements in orthogonal theory, $V_{ij}$, by

$$H_{ij} = V_{ij} \left( 1 + \frac{1}{K} S_{ij}^2 \right),$$

(11)

where

$$S_{ij} = (S_{ss\sigma} - 2(3S_{sp\sigma} - 3S_{pp\sigma}))/4$$

(12)

is the nonorthogonality between $sp^3$ hybrids.$^{19}$ The quantities $S_{\lambda\lambda',\mu}$ in turn are determined from

$$S_{\lambda\lambda',\mu} = \frac{2V_{\lambda\lambda',\mu}}{K(\epsilon_\lambda + \epsilon_{\lambda')}}.$$

(13)

We further introduce a simple distance dependence in the nonorthogonality coefficient, $K$,

$$K(r) = K_0 e^{\alpha(r-d_0)^2}.$$

(14)

This modification is similar in spirit to Anderson’s$^{21}$ modification to the extended Hückel method. As shown later this dependence yields better transferability for bond lengths and vibrational frequencies by giving improved agreement at both the cluster and bulk ends.

A. Dynamical matrix

The dynamical matrix is defined by

$$F_{i,j} = \frac{1}{(m_i m_j)^{1/2}} \left[ \frac{\partial^2 U}{\partial x_i \partial x_j} \right]_0 = \frac{1}{(m_i m_j)^{1/2}} \left[ \sum_{n=1}^{occ} \left( \frac{\partial^2 E_n}{\partial x_i \partial x_j} \right)_0 \right] + \left( \frac{\partial^2 U_{rep}}{\partial x_i \partial x_j} \right)_0.$$

(15)

Here $i,j = 1,..,3N$, where $N$ is the number of atoms in the cluster. In Appendix A we derive the following explicit expression for the analytic second derivative of the eigenvalues $E_n$:

$$
\begin{align*}
\sum_{n=1}^{occ} \frac{\partial^2 E_n}{\partial x_i \partial x_j} &= \sum_{n=1}^{occ} \mathbf{C}^n \left[ \frac{\partial \mathbf{H}}{\partial x_i} - E_n \frac{\partial \mathbf{S}}{\partial x_i} \right] \mathbf{C}^\dagger \mathbf{C}^n - \sum_{n=1}^{occ} \sum_{m=1}^{occ} \left[ \mathbf{C}^m \left( \frac{\partial \mathbf{H}}{\partial x_i} - E_n \frac{\partial \mathbf{S}}{\partial x_i} \right) \mathbf{C}^\dagger \mathbf{C}^m \frac{\partial \mathbf{S}}{\partial x_j} \mathbf{C}^n + (i \leftarrow j) \right] \\
&+ \sum_{n=1}^{occ} \sum_{m=1}^{occ} \frac{1}{(E_n - E_m)^{1/2}} \left[ \mathbf{C}^m \left( \frac{\partial \mathbf{H}}{\partial x_i} - E_n \frac{\partial \mathbf{S}}{\partial x_i} \right) \mathbf{C}^\dagger \mathbf{C}^m \frac{\partial \mathbf{S}}{\partial x_j} \mathbf{C}^n + (i \leftarrow j) \right].
\end{align*}
$$

(16)
(i ↔ j) denotes interchange of the indices i and j of the terms in the square brackets. Note that in the orthogonal case, \( \partial S / \partial x_i = 0 \). The second and the third term on the right-hand side of Eq. (16) which involve two sums over occupied states, are a unique feature of the nonorthogonal scheme.

### III. RESULTS

In this section we present our results obtained using the GTBMD scheme. All the results are obtained without introducing any artificial cutoff in the interactions. In practice for crystals, this is achieved by increasing the shell size until results remain unchanged. We find inclusion of up to the third neighbor shell (corresponding to a cutoff of 5 Å) to be sufficient for obtaining converged results. The parameters used are listed in Tables I and II. In determining these parameters, we treat \( K_0, \sigma, x_0, \) and \( a \) as adjustable, requiring a reasonable fit to all properties across sp\(^2\) phases of carbon. Geometry optimization in all cases was done by damped molecular dynamics relaxation from various starting points.

#### A. C\(_{60}\)

We find the two different bond lengths in C\(_{60}\) to be 1.40 and 1.45 Å on relaxation, which is in very good agreement with the experimental values of 1.402 and 1.462 Å, respectively.\(^{22}\) The vibrational frequencies of C\(_{60}\) are also determined using the scheme outlined in Sec. II A after the geometry is optimized using the GTBMD method. In Table III we present our results for the vibrational modes of C\(_{60}\) and compare with available experimental values. As seen from Table III, the agreement with experiment is excellent with an average deviation of only 6.7%. In Table III we also list the best theoretical estimation of all vibrational frequencies for C\(_{60}\) obtained using the LDA method.\(^{23}\) Our results show an average deviation of 13.6% from LDA results. The largest discrepancies occur for the intermediate frequency \( T_{2u} \) and \( T_{2g} \) modes. In view of the fact that our scheme makes use of molecular dynamics method for full geometry optimization while estimating the vibrational modes, while the LDA results quoted did not involve molecular dynamics optimization, the agreement must be considered very good.

#### B. C\(_{70}\)

The C\(_{70}\) molecule has \( D_{5h} \) symmetry [Fig. 1(b)]. The bond lengths range from 1.392 Å to 1.449 Å. The lower symmetry of C\(_{70}\), when compared to C\(_{60}\), gives rise to a large number of allowed infrared and Raman active modes for this molecule, making a direct comparison with experi-

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**TABLE II. Adjustable parameters for carbon.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_0 )</td>
<td>2.9</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>3.0 Å(^{-2})</td>
</tr>
<tr>
<td>( \phi_0 )</td>
<td>0.89 eV</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>1.8 Å(^{-1})</td>
</tr>
</tbody>
</table>

**TABLE III. Vibrational frequencies for the pristine fullerene molecule (cm\(^{-1}\)).**

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Experiment (^a)</th>
<th>Present work</th>
<th>LDA (^b)</th>
<th>Symmetry</th>
<th>Experiment</th>
<th>Present work</th>
<th>LDA (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>496 1470</td>
<td>475 1451</td>
<td>483 1529</td>
<td>( A_u )</td>
<td>948</td>
<td>947</td>
<td></td>
</tr>
<tr>
<td>( T_{1g} )</td>
<td>417 800 1256</td>
<td>566 825 1292</td>
<td>( T_{1u} )</td>
<td>527 1183 1428</td>
<td>558 1152 1424</td>
<td>548 1214 1485</td>
<td></td>
</tr>
<tr>
<td>( T_{2g} )</td>
<td>250 527 794 1387</td>
<td>550 771 795 1360</td>
<td>( T_{2u} )</td>
<td>308 1220 1461</td>
<td>344 1227 1558</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( G_x )</td>
<td>423 527 564 1088 1330 1465</td>
<td>484 564 763 1117 1326 1528</td>
<td>( G_u )</td>
<td>316 399 738 1117 1338 1443</td>
<td>356 758 1214 1339 1467</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_x )</td>
<td>273 437 710 774 1099 1250 1428 1575</td>
<td>239 369 581 732 1075 1232 1412 1534</td>
<td>( H_u )</td>
<td>263 432 713 778 1111 1282 1469 1598</td>
<td>263 432 713 778 1111 1282 1469 1598</td>
<td>362 396 449 558 650 1172 1343 1532</td>
<td>396 534 742 1230 1358 1588</td>
</tr>
</tbody>
</table>

\(^a\)Reference 11.
\(^b\)Reference 23.
ment rather difficult. Since the present scheme does not require the molecule to have a high degree of symmetry for expediting the calculation, we easily obtain all the vibrational modes, which are listed in Table IV. In Table IV we also list some of the experimentally available frequencies for comparison. No LDA calculations have been reported, although semiempirical calculations have been performed.

C. C₈₄

Unlike the highly symmetric C₆₀ and C₇₀ molecules, many stable isomers are possible for C₈₄. We examine two structures for this cluster, namely a $D_{6h}$ [Fig. 1(c)] and a $T_d$ geometry. The $D_{6h}$ structure can be thought of as being similar to C₇₀ with the fivefold rotation axis replaced by a sixfold axis. The $T_d$ cluster contains four hexagons that are completely surrounded by other hexagons. Additionally, it also has four hexagons with three pentagons adjacent to them. On relaxation using our molecular dynamics scheme, we find the $D_{6h}$ cluster to be more stable than the $T_d$ geometry by 0.91 eV. This agrees with the reported MNDO and HF/3-21G results. The bond lengths for the $D_{6h}$ cluster range from 1.369 to 1.451 Å. The vibrational frequencies for this molecule are easily obtained using our scheme, and are listed in Table V. MNDO results have been reported and lie in the same range.

D. Carbon nanotubes

The discovery of carbon nanotubes with unusual geometric and electronic properties has generated considerable interest. These tubes can be visualized as graphitic sheets rolled up into cylinders giving rise to quasi-one-dimensional structures. Since their discovery, many theoretical efforts have focused on various interesting properties of these novel materials. Recently, experimentalists have succeeded in producing nanotubes with radius as small as 7 Å, roughly that of the diameter of C₆₀. Interestingly, these tubes ex-

![Fig. 1. Relaxed geometries for (a) C₆₀, (b) C₇₀, and (c) C₈₄ ($D_{6h}$).](image-url)
hibit metallic or semiconducting character depending on the helical arrangements of the carbon atoms. The finite tubes are expected to undergo Jahn–Teller distortions whose effect on the electronic structure could be significant.

In this work we examined two nanotubes with differing configurations. Each tube had a radius of 7.1 Å and consisted of 150 carbon atoms. Tube A was constructed by taking two layers of carbon atoms forming the equatorial belt of the C_{70} fullerene and repeating them to obtain an extended structure resulting in a hollow tube. The ends of the tube are then terminated by placing the polar caps of C_{70}, resulting in a D_{5h} structure [Fig. 2(a)]. This structure contains a series of carbon–carbon bonds perpendicular to the tube axis. Tube B was obtained by rotating the hexagons forming the hollow of tube A by 90° and terminating the ends by placing a polar cap with threefold rotation symmetry (hexagon surrounded by alternating hexagons and pentagons), resulting in a D_{3h} structure [Fig. 2(b)]. In this tube there are a series of carbon–carbon bonds parallel to the tube axis.

Tube A showed no appreciable Jahn–Teller distortions on relaxation using our molecular dynamics method. The relaxed structure was found to be metallic with no gap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO). The bond lengths for this tube range from 1.394 to 1.451 Å. Tube B, however, showed considerable symmetry lowering Jahn–Teller distortions. The relaxed structure was found to be semiconducting, with a gap of 0.7 eV. Both the highest occupied and lowest unoccupied molecular orbital states for the relaxed structure were found to be nondegenerate. The bond length distribution showed larger dispersion than tube A, ranging from 1.379 to 1.452 Å. Tube B was found to be slightly more stable than tube A (by 0.5 eV). The slight energy difference gives strong indication that molecular dynamics techniques, allowing for full symmetry unconstrained relaxation, are essential when exploring the stabilities of various isomers of nanotubes.

Evaluation of the vibrational modes for the 150 atom carbon nanotube is straightforward and fast with the scheme outlined in Sec. II A. In Table VI we list all the modes for tube B. The frequencies range from 81 to 1568 cm^{-1}. It is interesting to note that the lowest frequency mode in going from C_{60} through C_{70}, C_{84} (D_{6h}), and C_{120} (tube) takes on values of 239, 203, 184, and 81 cm^{-1}, respectively. An ex-
amination of the eigenvectors of these lowest frequency modes reveals that in C\textsubscript{70} and in tube B the mode has longitudinal nodes in the cap regions and two transverse nodes around the belt. It is clear that a breathing motion of the cylindrical part of the tube would have a higher restoring force due to the resulting bond stretches in the cap region. The softening of this mode in going from C\textsubscript{70} to tube B may be understood in terms of the increase in the wavelength of this mode.

E. Graphite

To demonstrate the transferability of our scheme, we next consider a graphite sheet. Graphite is a prototype sp\textsuperscript{2} covalent solid, with two atoms in the unit cell, with nearest-neighbor bond length less than the sum of the covalent radii of the carbon atoms. It possesses layered structure with considerable differences in the in- and out-of-plane interactions. Here we present results for a single layer of atoms since the interplanar interaction is not a covalent interaction. We obtain a nearest-neighbor bond length of 1.42 Å, identical to the experimental value of 1.42 Å\textsuperscript{40}. The computed band structure is shown in Fig. 3 and is in good agreement with accepted band structure calculations.\textsuperscript{18}

Accurate theoretical lattice dynamics studies of graphite almost always rely on parametrization of the force constants for constructing the dynamical matrix for frequency evaluation. To our knowledge, no first principles results have been reported. We can easily construct the dynamical matrix for graphite using the scheme outlined in Sec. II A. Special point averaging is done for Brillouin zone integration by taking 18\textsuperscript{k}-points in the irreducible two-dimensional zone. We obtain a value of 1588 cm\textsuperscript{-1} for the E\textsubscript{2g} mode, in excellent agreement.
agreement with the experimental value of 1582 cm$^{-1}$.$^{40,41}$ For the $A_{2u}$ mode, we calculate a value of 695 cm$^{-1}$, in reasonable agreement with the corresponding experimental value of 868 cm$^{-1}$.$^{40,41}$

**IV. SUMMARY**

We have presented a minimal parameter generalized tight-binding scheme suitable both for geometry optimization by molecular dynamics, and vibrational calculations, for $sp^2$ forms of carbon. Our work demonstrates that inclusion of nonorthogonality in tight-binding theory in conjunction with a judicious choice of parameters can provide results in good agreement with experiment. The scheme is considerably faster than ab initio or LDA methods and readily allows vibrational frequency estimations for large clusters with low symmetry, not accessible by ab initio methods. This has been achieved by incorporating very few parameters and a simple scaling with distance of the parameters.

**ACKNOWLEDGMENTS**

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**APPENDIX: CONSTRUCTION OF THE DYNAMICAL MATRIX**

In this Appendix we describe the determination of the second derivative of the eigenvalues $E_n$. We define

$$D_x^a C^n + D^a \frac{\partial C^n}{\partial x_i} = 0,$$

(A2)

where

$$D^a = \frac{\partial D^a}{\partial x_i} = \frac{\partial H}{\partial x_i} - E_n \frac{\partial S}{\partial x_i} - \frac{\partial E_n}{\partial x_i} S.$$

(A3)

Differentiating Eq. (A2) with respect to $x_j$ we get

$$\frac{\partial^2 E_n}{\partial x_i \partial x_j} SC^n = D_{x_i}^a C^n + D^a \frac{\partial C^n}{\partial x_j} + D^a \frac{\partial C^n}{\partial x_j} + D^a \frac{\partial^2 C^n}{\partial x_i \partial x_j},$$

(A4)

with

$$D_{x_i}^a \frac{\partial C^n}{\partial x_j} = \frac{\partial^2 H}{\partial x_i} \frac{\partial E_n}{\partial x_j} - \frac{\partial E_n}{\partial x_i} \frac{\partial S}{\partial x_j} - E_n \frac{\partial^2 S}{\partial x_i \partial x_j},$$

(A5)

where we have made use of the normalization property of $C^n$ [Eq. (6)]. Multiplying Eq. (A4) on the left with $C^{\dagger n}$ and using the fact that $C^{\dagger n} D^n = 0$, we get

$$\frac{\partial^2 E_n}{\partial x_i \partial x_j} C^{\dagger n} + C^{\dagger n} D_{x_j}^a C^n + C^{\dagger n} D^a \frac{\partial C^n}{\partial x_j} + C^{\dagger n} D^a \frac{\partial^2 C^n}{\partial x_i \partial x_j}.$$  

(A6)

From Eq. (A2) we have

$$D^a \frac{\partial C^n}{\partial x_j} = - D_{x_j}^a C^n.$$  

(A7)

The completeness relation is

$$\sum_m SC^{\dagger n} C^m = 1.$$  

(A8)

Since $C^{\dagger n} D^n (SC^n/\partial x_i) = 0$, the right-hand side of Eq. (A7) has no projection in the degenerate manifold of $C^n$. Thus we can write Eq. (A7) as

$$D^a \frac{\partial C^n}{\partial x_j} = - PD_{x_j}^a C^n,$$

(A9)

where

$$P = 1 - SC^{\dagger n} C^n = \sum_{m \neq n} SC^m C^{\dagger m}.$$  

(A10)

Using Eq. (A10) in Eq. (A9) for $P$ and multiplying both sides of Eq. (A9) on the left by $(D^n)^{-1}$ we get,

$$\frac{\partial C^n}{\partial x_i} = - \frac{1}{(E_n - E_m)} D^n_{x_i} C^n,$$

(A11)

where

$$D^n_{x_i} = \frac{\partial H}{\partial x_i} - E_n \frac{\partial S}{\partial x_i},$$

(A12)

and we have used the fact that for $m \neq n$, $C^{\dagger n} SC^n = 0$. Thus, the second term on the right-hand side of Eq. (A6) becomes

$$C^{\dagger n} D^n_{x_i} \frac{\partial C^n}{\partial x_j} = \sum_{m \neq n} \frac{1}{(E_n - E_m)} C^{\dagger n} D^n_{x_i} C^n C^{\dagger m} D^n_{x_j} C^m.$$  

(A13)
where again we have used the fact that for \( m \neq n \), 
\[ C_m^{\dagger}SC_n = 0. \]
Using this in Eq. (A6) we have,
\[
\frac{\partial^2 E_n}{\partial x_i \partial x_j} = C_n^{\dagger}D_{n, i, j}C_n + \sum_{m \neq n} \frac{1}{E_n - E_m} \times [C_m^{\dagger}D_{n, j}C_m + \delta S \frac{\partial S}{\partial x_j} C_n + (i \leftrightarrow j)],
\]
(A14)
where \((i \leftrightarrow j)\) denotes interchange of the indices \(i\) and \(j\) of the terms in the square bracket. Next we sum Eq. (A14) over occupied levels \(n\) and separate the sum over \(m\) in the second term into sums over occupied and unoccupied states, i.e.,
\[
\sum_{n} \sigma \frac{\partial^2 E_n}{\partial x_i \partial x_j} = \sum_{n} C_n^{\dagger}D_{n, i, j}C_n + \sum_{m \neq n} \sum_{\sigma \sigma'} \left[ \cdots \right]
\]
\[
+ \sum_{n} \sum_{\sigma \sigma'} \left[ \cdots \right].
\]
(A15)
After some algebra it can be shown that
\[
\sum_{n} \sum_{\sigma \sigma'} \left[ \cdots \right] = \sum_{n} \sum_{\sigma \sigma'} \left[ C_n^{* \dagger}D_{n, j}C_n^{\dagger} \frac{\partial S}{\partial x_j} C_n + (i \leftrightarrow j) \right].
\]
(A16)
We rewrite the first term on the right-hand side in Eq. (A15) as
\[
\sum_{n} C_n^{\dagger}D_{n, i, j}C_n = \sum_{n} C_n^{* \dagger}D_{n, j}C_n^{\dagger} + \sum_{\sigma \sigma'} \left[ \cdots \right],
\]
\[
+ \sum_{n} \left[ C_n^{* \dagger} \frac{\partial E_n}{\partial x_i} \frac{\partial S}{\partial x_i} C_n - (i \leftrightarrow j) \right].
\]
(A17)
where
\[
\hat{D}_{n, i, j} = \frac{\partial^2 H}{\partial x_i \partial x_j} - E_n \frac{\partial^2 S}{\partial x_i \partial x_j}.
\]
(A18)
Now, from the cross terms of Eq. (A5) we get
\[
\sum_{n} \left( C_n^{* \dagger} \frac{\partial E_n}{\partial x_i} \frac{\partial S}{\partial x_j} C_n + (i \leftrightarrow j) \right) = \sum_{n} \sum_{m \neq n} \left[ \cdots \right],
\]
(A19)
where we have used Eq. (5) for the derivative \( \partial E_n / \partial x_i \). This term combines with \( \Sigma_{n} \Sigma_{m \neq n} \left[ \cdots \right] \) of Eq. (A15) to give
\[
\sum_{n} \left( C_n^{* \dagger} \frac{\partial E_n}{\partial x_i} \frac{\partial S}{\partial x_j} C_n + (i \leftrightarrow j) \right) + \sum_{n} \sum_{m \neq n} \left[ \cdots \right]
\]
\[
= \sum_{n} \sum_{m \neq n} \left( C_n^{* \dagger} \hat{D}_{n, j}C_m^{\dagger} \frac{\partial S}{\partial x_j} C_m + (i \leftrightarrow j) \right).
\]
(A20)
Collecting all the terms together, we get, for the electronic part of the second derivative,
\[
\sum_{n} \frac{\partial^2 E_n}{\partial x_i \partial x_j} = \sum_{n} \delta_{n \sigma} \frac{\partial S}{\partial x_j} C_n + (i \leftrightarrow j).
\]
(A21)
When Eq. (A1) is substituted back into Eq. (A21), we get Eq. (16).