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Ab initio evaluation of the Born correction, Born couplings, and higher derivative matrix elements with Gaussian-lobe orbitals

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Formulation of the expectations of eight operators required for the evaluation of the Born corrections, the Born couplings, and higher derivatives of the Born–Oppenheimer wave functions are derived for the case of a Gaussian-lobe orbital (GLO) basis. The relative simplicity of these analytical formulas is a special advantage of GLO and reduces the computer time in these calculations. Some operators treated here require a modification of the Slater rules. As examples of applications of these techniques, *ab initio* calculations of the orbital stresses and the Born corrections for the ground state $X\,^1\Sigma_g^+$ and excited states $^1\Sigma_g^+$ (*II*), C, $C'\,^3\Pi_u$, and $^3\Pi_u$ (*II*) of N_2 are reported. The obtained results show that the Born correction near the avoided crossing region strongly depends upon the nuclear separation; in this region configuration interaction makes an important contribution.

I. INTRODUCTION

Born–Oppenheimer (BO) adiabatic potential-energy surfaces[1] for molecules and collision complexes are essential to the interpretation of molecular properties and provide a description of the dynamics of nuclei in processes involving essentially a single electronic state. On the other hand, the study of radiationless transitions, predissociation, electronic transitions in molecular collisions, and certain perturbations of molecular spectra requires a nonadiabatic treatment. The inclusion of the Born (nonadiabatic) coupling parameters[2] in the Hamiltonian allows treatment of the breakdown of the BO approximation. These parameters are the matrix elements of the first derivative of the nuclear displacement operator (NDO) in the space spanned by the Born–Oppenheimer electronic wave functions (BOEWF). The properties of the NDO have been recently discussed in detail.[3]

There has been increasing interest in the study and calculation of the diagonal elements (the so-called Born correction terms),[4–12] off-diagonal elements (the so-called Born couplings),[11–20] and higher derivatives of the BO potential energy surfaces.[21] Since these matrix elements are generally considered difficult to calculate, several searches for a practically effective procedure to obtain these quantities are underway.[7–21] Algorithms for calculating first and second derivatives from large-scale configuration interaction (CI) molecular wave functions have been developed by Buenker and Peyerimhoff and their co-workers.[22]

Gaussian-lobe orbitals (GLO), first introduced by Preuss[23] and by Whitten[24,25] have been widely and successfully used in many molecular calculations.[26] This choice of basis has two main advantages: first, the formulas for expectations of various operators are relatively simple in terms of the GLO; second, less computation time is generally required—a nontrivial consideration for calculation of the Born corrections, the Born couplings, and the higher derivatives. Since these calculations involve many different operators, and reliable results require several full calculations of electronic wave functions, the advantage of the GLO basis is particularly well demonstrated in the present applications.

In this paper we derive the formulas for the expectations of the required operators in the GLO basis. The effectiveness of the method is evident from the accuracy and consistency of the results we report for the orbital stress and for the Born corrections for the ground state and several excited electronic states of N_2.

II. EXPECTATION VALUES REQUIRED FOR THE BORN COUPLINGS, THE BORN CORRECTIONS, AND HIGHER DERIVATIVES

We consider the following expectation values of the operators required for the evaluation of the Born correction, the Born couplings, and higher derivatives, in the space of BOEWF:

$$\langle\Psi_i|\left(\frac{\partial}{\partial Q}V\right)|\Psi_j\rangle, \tag{1}$$

$$\langle\Psi_i|\left(\frac{\partial^2}{\partial Q^2}V\right)|\Psi_j\rangle, \tag{2}$$

$$\langle\Psi_i|\left(\frac{\partial^3}{\partial Q^3}V\right)|\Psi_j\rangle, \tag{3}$$

$$\langle\Psi_i|\left(\frac{\partial^4}{\partial Q^4}V\right)|\Psi_j\rangle, \tag{4}$$

$$\langle\Psi_i|\frac{\partial}{\partial Q}|\Psi_j\rangle, \tag{5}$$

$$\langle\Psi_i|\frac{\partial^2}{\partial Q^2}|\Psi_j\rangle, \tag{6}$$

$$\left\langle\frac{\partial}{\partial Q}\Psi_i\middle|\frac{\partial}{\partial Q}\Psi_j\right\rangle, \tag{7}$$

$$\langle\Psi_i|\sum_{p,q}\nabla_p\cdot\nabla_q|\Psi_j\rangle, \tag{8}$$

where Q is an arbitrary generalized nuclear position coordinate. Indices p, q run over all electrons, $|\Psi_i\rangle$ and $|\Psi_j\rangle$ are BO electronic states, and V is the electron–nuclear potential-energy operator:

$$V=\sum_p V_p=-\sum_p\frac{Z_p}{r_p},$$

where Z_p is the charge number of the pth nucleus.

Operator (1) is used to calculate the vector Born coupling matrix elements by the Hellmann–Feynman formula,[3,28] the orbital stress, and the transition stress[28,29] and is useful in a force analysis for molecules.[30]

Operator (2) is used to calculate the Born correction parameters and the scalar Born coupling parameters by the Hellmann–Feynman formula[27] and its diagonal elements are related to the molecular force constants.

Operators (3) and (4) are used to evaluate the higher derivatives by the generalized Hellmann–Feynman formulas[3] and molecular cubic as well as quartic force constants.

Operator (5) is used to calculate the vector Born coupling parameter by the numerical method,[17,18] and also the nuclear contribution to the dipole transition moment between state i and state j.

Operator (6) can be used to obtain the Born correction parameters (diagonal elements) and the scalar Born coupling parameters (off-diagonal elements). Operator (7) provides another approach to the Born correction parameters, as suggested by Sellers and Pulay.[7,8] Besides this, it also serves as a consistency check for the numerical results of expectations for operator (6).[38]

The expectations of operator (8) are the cross terms of the electronic kinetic energy, which contribute to the total Born corrections and Born couplings.

III. THE TRANSFORMATION OF EXPECTATIONS FROM CI WAVE FUNCTION TO THE GLO BASIS

CI electronic wave functions $|i\rangle$ or Ψ_i at a nuclear configuration Q are the linear combinations of Slater determinant wave functions Φ_α:

$$\Psi_i(Q) = \sum_\alpha C_{i\alpha}(Q)\Phi_\alpha(Q), \qquad (9)$$

where CI coefficients $C_{i\alpha}$ are Q dependent as are the Slater determinants

$$\Phi_\alpha(Q) = (N!)^{-1/2} \, \text{Det}|\phi_{\alpha_1}(q_1,Q)\phi_{\alpha_2}(q_2,Q)\cdots$$

$$\times \phi_{\alpha_p}(q_p,Q)\cdots\phi_{\alpha_N}(q_N,Q)|. \qquad (10)$$

In Eq. (10) ϕ_p is the pth molecular orbital, which is the linear combination of primitive basis functions χ_i:

$$\phi_p(Q) = \sum_i c_{pi}(Q)\chi_i. \qquad (11)$$

The Q dependency of χ_i is reflected through the assignment of basis centers.

The functions χ_i are linear combinations of M Gaussian components. According to the GLO approach, the latter are the linear combinations of lobes which always are s-type Gaussians whose centers are located around the basis center A (see Refs. 24 and 25):

$$\chi_i(A) = \sum_{m=1}^{M} \sum_{k=1}^{L} (-1)^{k+1} d_{im} N_m \exp(-a_m r^2_{A_{mk}}), \qquad (12)$$

where M is the number of components, L is the number of lobes, which is equal to 1, 2, and 4 for s-, p-, and d-type basis functions, respectively. d_{im} is the normalized combination

coefficients of the mth component, a_m and N_m are the exponent and the normalization constant of the mth component, respectively, A_{mk} is the center of the kth lobe in the mth component, which is displaced from the basis center A for p and d functions. The magnitudes of these displacements of lobe centers are the same for a given component, but different lobes are displaced in different directions.[24–26]

The overlap integral between two basis functions $\chi_i(A)$ and $\chi_j(B)$ is

$$W_{ij} = \langle \chi_i(A)|\chi_j(B)\rangle = \sum_{mnkl} W^{(ij)}_\tau, \qquad (13)$$

where we use the collective subscript τ to represent the subscripts $mnkl$, and the lobe overlap integrals $W^{(ij)}_\tau$ are

$$W^{(ij)}_\tau = (-1)^{k+l} d_{im} d_{jn} N_m N_n \left(\frac{\pi}{a_m + b_n}\right)^{3/2}$$

$$\times \exp(-\sigma_{mn}|A_{mk}B_{nl}|^2), \qquad (14)$$

where $\sigma_{mn} = a_m b_n/(a_m + b_n)$, $|A_{mk}B_{nl}| = |\mathbf{B}_{nl} - \mathbf{A}_{mk}|$ and $\mathbf{A}_{mk}$ is the center of the kth lobe of the mth component of the ith basis function.

Operators (1)–(4) are ordinary one-electron operators. Operator (8) is an ordinary separable two-electron operator. The transformation of expectations for these operators from CI wave functions to the GLO basis can be accomplished by straightforward application of the Slater rules.

However, operators (5)–(7) are special cases. In the transformation from CI wave functions to Slater determinants, it should be noted, as many authors have mentioned previously, that they are differential operators. Thus

$$\langle \Psi_i|\Psi_j'\rangle = \sum_\alpha C_{i\alpha} C'_{j\alpha} + \sum_{\alpha\beta} C_{i\alpha} C_{j\beta}\langle\Phi_\alpha|\Phi_\beta'\rangle, \qquad (15)$$

$$\langle \Psi_i|\Psi_j''\rangle = \sum_\alpha C_{i\alpha} C''_{j\alpha} + 2\sum_{\alpha,\beta} C_{i\alpha} C'_{j\beta}\langle\Phi_\alpha|\Phi_\beta'\rangle$$

$$+ \sum_{\alpha,\beta} C_{i\alpha} C_{j\beta}\langle\Phi_\alpha|\Phi_\beta''\rangle, \qquad (16)$$

$$\langle \Psi_i'|\Psi_j'\rangle = \sum_\alpha C'_{i\alpha} C'_{j\alpha} + \sum_{\alpha,\beta}[C'_{i\alpha} C_{j\beta}\langle\Phi_\alpha|\Phi_\beta'\rangle$$

$$+ C_{i\alpha} C'_{j\beta}\langle\Phi_\alpha'|\Phi_\beta\rangle] + \sum_{\alpha,\beta} C_{i\alpha} C_{j\beta}\langle\Phi_\alpha'|\Phi_\beta'\rangle. \qquad (17)$$

In the transformation of expectations from Slater determinants to molecular orbitals operator (5) complies with the Slater rule for one-electron operators, even though the operator itself does not contain any electronic coordinates. But the other two operators, which are "zero-electron operators," do not obey the standard Slater rule. Instead, they obey a rule that is similar to the Slater rule.

(1) If Φ_α and Φ_β are the same then

$$\langle \Phi_\alpha|\Phi_\beta''\rangle = \sum_p \langle\phi_p|\phi_p''\rangle + \sum_{p\neq q} (\langle\phi_p|\phi_q'\rangle)^2, \qquad (18)$$

$$\langle \Phi_\alpha'|\Phi_\beta'\rangle = \sum_p \langle\phi_p'|\phi_p'\rangle - \sum_{p\neq q} (\langle\phi_p|\phi_q'\rangle)^2, \qquad (19)$$

where the prime refers to derivative with respect to a nuclear coordinate. Equation (19) was pointed out previously by Sellers and Pulay.[7]

(2) If Φ_α and Φ_β differ in only one orbital, after a suitable permutation they may be written as

$$\Phi_\alpha = |\phi_1\phi_2\cdots\phi_{k-1}\phi_r|,$$

$$\Phi_\beta = |\phi_1\phi_2\cdots\phi_{k-1}\phi_s|,$$

where $r \neq s$. In this case

$$\langle\Phi_\alpha|\Phi_\beta''\rangle = \langle\phi_r|\phi_s''\rangle + 2\sum_{m=1}^{k-1}\langle\phi_m|\phi_s'\rangle\langle\phi_m|\phi_r'\rangle), \quad (20)$$

$$\langle\Phi_\alpha'|\Phi_\beta'\rangle = \langle\phi_r'|\phi_s'\rangle - 2\sum_{m=1}^{k-1}\langle\phi_m|\phi_s'\rangle\langle\phi_m|\phi_r'\rangle). \quad (21)$$

(3) If Φ_α and Φ_β differ in two orbitals, after a suitable permutation they may be written as

$$\Phi_\alpha = |\phi_1\phi_2\cdots\phi_{k-2}\phi_r\phi_u|,$$

$$\Phi_\beta = |\phi_1\phi_2\cdots\phi_{k-2}\phi_s\phi_v|.$$

so that we have

$$\langle\Phi_\alpha|\Phi_\beta''\rangle = 2[\langle\phi_r|\phi_s'\rangle\langle\phi_u|\phi_v'\rangle - \langle\phi_r|\phi_v'\rangle\langle\phi_u|\phi_s'\rangle], \quad (22)$$

$$\langle\Phi_\alpha'|\Phi_\beta'\rangle = -2[\langle\phi_r|\phi_s'\rangle\langle\phi_u|\phi_v'\rangle - \langle\phi_r|\phi_v'\rangle\langle\phi_u|\phi_s'\rangle]. \quad (23)$$

(4) If Φ_α and Φ_β differ in three or more orbitals, $\langle\Phi_\alpha|\Phi_\beta''\rangle$ and $\langle\Phi_\alpha'|\Phi_\beta'\rangle$ vanish.

In the last transformation, that of expectations from molecular orbitals to the GLO basis, operators (5)–(7) have similar transformations to those from CI wave functions to Slater determinants:

$$\langle\phi_p|\phi_q'\rangle = \sum_{i,j} c_{pi}c_{qj}'\langle\chi_i|\chi_j\rangle + \sum_{i,j} c_{pi}c_{qj}\langle\chi_i|\chi_j'\rangle, \quad (24)$$

$$\langle\phi_p|\phi_q''\rangle = \sum_{i,j} c_{pi}c_{qj}''\langle\chi_i|\chi_j\rangle + 2\sum_{i,j} c_{pi}c_{qj}'\langle\chi_i|\chi_j'\rangle$$

$$+ \sum_{i,j} c_{pi}c_{qj}\langle\chi_i|\chi_j''\rangle, \quad (25)$$

$$\langle\phi_p'|\phi_q'\rangle = \sum_{i,j} c_{pi}'c_{qj}'\langle\chi_i|\chi_j\rangle$$

$$+ \sum_{i,j} [c_{pi}'c_{qj}\langle\chi_i|\chi_j'\rangle + c_{pi}c_{qj}'\langle\chi_i'|\chi_j\rangle]$$

$$+ \sum_{i,j} c_{pi}c_{qj}\langle\chi_i'|\chi_j'\rangle. \quad (26)$$

On the other hand, the generalized coordinates Q are linear combinations of nuclear coordinates, and transformation from these generalized coordinates to the ordinary Cartesian coordinates, which are used in most quantum chemistry programs, produces cross terms. Taking all of the results into account, we finally arrive at the following expectations of these operators in the GLO basis:

$$\langle\chi_i(A)|(\nabla_C V)|\chi_j(B)\rangle, \quad (27)$$

$$\langle\chi_i(A)|(\nabla_D\nabla_C V)|\chi_j(B)\rangle, \quad (28)$$

$$\langle\chi_i(A)|(\nabla_E\nabla_D\nabla_C V)|\chi_j(B)\rangle, \quad (29)$$

$$\langle\chi_i(A)|(\nabla_F\nabla_E\nabla_D\nabla_C V)|\chi_j(B)\rangle, \quad (30)$$

$$\langle\chi_i(A)|\nabla_C|\chi_j(B)\rangle, \quad (31)$$

$$\langle\chi_i(A)|\nabla_D\nabla_C|\chi_j(B)\rangle, \quad (32)$$

$$\langle\nabla_D\chi_i(A)|\nabla_C\chi_j(B)\rangle, \quad (33)$$

$$\langle\chi_i(A)|\nabla|\chi_j(B)\rangle, \quad (34)$$

where the expectation of Eq. (34) originates from operator (8) since it is a separable two-electron operator.

IV. EVALUATION OF EXPECTATIONS IN THE GLO BASIS

For convenience, the lobe functions at the center A_{mk} are written as

$$|a_m, A_{mk}\rangle = \exp(-a_m r_{A_{mk}}^2).$$

The two-lobe integrals that appear in the electron–nuclear attractive potentials are

$$\langle a_m, A_{mk}|1/r_C|b_n, B_{nl}\rangle = K_\tau F_0(t_\tau), \quad (35)$$

where $\mathbf{r}_C$ is the position of the electron with the nucleus C as origin and

$$K_\tau = \frac{2\pi}{a_m + b_n}\exp(-\sigma_{mn}|A_{mk}B_{nl}|^2), \quad (36)$$

$$\sigma_{mn} = \frac{a_m b_n}{a_m + b_n}, \quad (37)$$

$$F_0(t) = \int_0^1 e^{-tu^2}\,du = \frac{1}{\sqrt{t}}\int_0^{\sqrt{t}} e^{-u^2}\,du, \quad (38)$$

$$t_\tau = (a_m + b_n)|\mathbf{C} - \mathbf{P}_\tau|^2, \quad (39)$$

and

$$\mathbf{P}_\tau = \frac{a_m\mathbf{A}_{mk} + b_n\mathbf{B}_{nl}}{a_m + b_n}. \quad (40)$$

The subscripts $\tau = mnkl$, indicate that K, t, and P are lobe-pair dependent. The function $F_0(t)$ of Eq. (38) is the special case of the error functions with $m = 0$:

$$F_m(t) = \int_0^1 u^{2m}e^{-tu^2}\,du \quad (40a)$$

that obey the recursion relation

$$\frac{\partial}{\partial t}F_m(t) = -F_{m+1}(t). \quad (41)$$

Combination of Eqs. (12) and (35) gives the three-center potential integrals

$$\langle\chi_i(A)|V_C|\chi_j(B)\rangle$$

$$= -Z_C\sum_{mnkl}(-1)^{k+1}d_{im}d_{jn}N_m N_n K_\tau F_0(t_\tau), \quad (42)$$

where t_τ depends on all three centers A, B, and C and K depends on A and B.

A. $\langle\chi_i(A)|(\nabla_C V)/\chi_j(B)\rangle$

For the simplest case, $C \neq B$ and $C \neq A$ it is evident that

$$\langle\chi_i(A)|\nabla_C V|\chi_j(B)\rangle = \nabla_C[\langle\chi_i(A)|V_C|\chi_j(B)\rangle]$$

$$= Z_C\sum_{mnkl}(-1)^{k+1}d_{im}d_{jn}N_m N_n K_\tau F_1(t_\tau)[\nabla_C t_\tau]. \quad (43)$$

Using Eq. (39) and the lobe overlap integrals shown in Eq. (14), we have

$$\langle \chi_i(A)|\nabla_C V|\chi_j(B)\rangle$$

$$= -4Z_C \sqrt{\frac{1}{\pi}} \sum_{mnkl} (a_m + b_n)^{3/2}$$

$$\times W_\tau^{(ij)} F_1(t_\tau)(\mathbf{C} - \mathbf{P}_\tau). \tag{44}$$

If $C = B \neq A$ the situation is not as obvious as the above case:

$$\langle \chi_i(A)|(\nabla_B V)|\chi_j(B)\rangle = \langle \chi_i(A)|(\nabla_B V_B)|\chi_j(B)\rangle$$

$$= \nabla_B[\langle \chi_i(A)|V_B|\chi_j(B)\rangle] - \langle \chi_i(A)|V_B \nabla_B|\chi_j(B)\rangle. \tag{45}$$

The first term on the right-hand side is easy to obtain by taking the gradient of Eq. (42) with respect to the coordinates of nucleus B. However, it is important to realize that both K_τ and t_τ are dependent upon the coordinates of nucleus B:

$$\nabla_B[\langle \chi_i(A)|V_B|\chi_j(B)\rangle]$$

$$= -Z_B \sum_{mnkl} (-1)^{k+l} d_{im} d_{jn} N_m N_n$$

$$\times [(\nabla_B K_\tau) F_0(t_\tau) - K_\tau F_1(t_\tau)(\nabla_B t_\tau)]$$

$$= -4Z_B \sqrt{\frac{1}{\pi}} \sum_{mnkl} (a_m + b_n)^{1/2} W_\tau^{(ij)}$$

$$\times [b_n(\mathbf{B}_{nl} - \mathbf{P}_\tau) F_0(t_\tau) + a_m(\mathbf{B} - \mathbf{P}_\tau) F_1(t_\tau)]. \tag{46}$$

Using the general formula for attractive integrals of Cartesian Gaussians[35-37] we have the second term of Eq. (45):

$$\langle \chi_i(A)|V_B|\nabla_B \chi_j(B)\rangle$$

$$= -4Z_B \sqrt{\frac{1}{\pi}} \sum_{mnkl} (a_m + b_n)^{1/2} W_\tau^{(ij)}$$

$$\times [b_n(\mathbf{B}_{nl} - \mathbf{P}_\tau) F_0(t_\tau) - b_n(\mathbf{B} - \mathbf{P}_\tau) F_1(t_\tau)].$$

Combining this equation and Eq. (46) and using Eq. (14) we obtain

$$\langle \chi_i(A)|\nabla_B V|\chi_j(B)\rangle$$

$$= -4Z_B \sqrt{\frac{1}{\pi}} \sum_{mnkl} (a_m + b_n)^{3/2}$$

$$\times W_\tau^{ij} F_1(t_\tau)(\mathbf{B} - \mathbf{P}_\tau). \tag{47}$$

If $C = A \neq B$ a similar result can be derived.

For the last case, $C = B = A$, we have

$$\langle \chi_i(A)|(\nabla_A V)|\chi_j(A)\rangle = \langle \chi_i(A)|(\nabla_A V_A)|\chi_j(A)\rangle$$

$$= \nabla_A[\langle \chi_i(A)|V_A|\chi_j(A)\rangle] - \langle \chi_i(A)|V_A \nabla_A|\chi_j(A)\rangle$$

$$- (\nabla_A \langle \chi_i(A)|)V_A|\chi_j(A)\rangle.$$

The first term on the right-hand side vanishes since a one-center integral is independent of the choice of origin. By the same procedure as the case of $C = B \neq A$, evaluating the remaining two terms we find that

$$\langle \chi_i(A)|\nabla_A V|\chi_j(A)\rangle$$

$$= -4Z_A \sqrt{\frac{1}{\pi}} \sum_{mnkl} (a_m + b_n)^{3/2}$$

$$\times W_\tau^{(ij)} F_1(t_\tau)(\mathbf{A} - \mathbf{P}_\tau). \tag{48}$$

Comparison of Eq. (44) with Eqs. (47) and (48) shows that they actually have the same form although they have

been obtained by different derivations. Therefore Eq. (44) is the correct form for the expectations for operator (1) in the GLO basis, disregarding the relations among A, B, and C. We also can write Eq. (44) as

$$\langle \chi_i(A)|\nabla_C V|\chi_j(C)\rangle$$

$$= -Z_C \sum_{mnkl} \lambda_{mn,1} W_\tau^{(ij)} F_1(t_\tau)(\mathbf{C} - \mathbf{P}_\tau), \tag{49}$$

where $\lambda_{mn,1}$ is the $k = 1$ case of the following defining expression:

$$\lambda_{mn,k} = 2^{k+1} \sqrt{\frac{1}{\pi}} (a_m + b_n)^{k+1/2}. \tag{50}$$

B. $\langle \chi_i(A)|\nabla_D \nabla_C V|\chi_j(B)\rangle$

This is a second-rank tensor operator with nine components. It is easy to see that the expectation vanishes unless $D = C$, so the nine components can be represented simply by the subscripts xx, yy, zz, xy, xz, yx, yz, zx, and zy.

For the simplest case of $C \neq B$, $C \neq A$, apparently we have

$$\langle \chi_i(A)|\nabla_D \nabla_C V|\chi_j(B)\rangle = \nabla_D \nabla_C \langle \chi_i(A)|\nabla_C|\chi_j(B)\rangle \delta_{DC}. \tag{51}$$

However, Eq. (51) does not involve the singularity at $\mathbf{r}_C$ which appears for this operator. Using the identity

$$\nabla_C^2 \frac{1}{r_C} = -4\pi\delta(\mathbf{r}_C)$$

$$= -4\pi\delta(x - X_C)\delta(y - Y_C)\delta(z - Z_C), \tag{52}$$

where x, y, and z are the electronic coordinates and X_C, Y_C, and Z_C are coordinates for nucleus C, we have the following expression for an arbitrary component $\alpha\beta$ of this operator:

$$[\langle \chi_i(A)|\nabla_D \nabla_C V|\chi_j(B)\rangle]_{\alpha\beta}$$

$$= [\nabla_D \nabla_C \langle \chi_i(A)|V_C|\chi_j(B)\rangle]_{\alpha\beta}\delta_{DC}$$

$$+ \frac{4\pi Z_C}{3}\langle \chi_i(A)|\delta(\mathbf{r}_C)|\chi_j(B)\rangle \delta_{\alpha\beta}\delta_{DC}. \tag{53}$$

By using Eqs. (42), (41), and (39), we found the first term on the right-hand side of the above equation to be

$$[\nabla_D \nabla_C \chi_i(A)|V_C|\chi_j(B)\rangle]_{\alpha\beta}\delta_{DC}$$

$$= -Z_C \sum_{mnkl} W_\tau^{(ij)}[\lambda_{mn,2} F_2(t_\tau)(\mathbf{C} - \mathbf{P}_\tau)_{\alpha\beta}$$

$$- \lambda_{mn,1} F_1(t_\tau)\delta_{\alpha\beta}]\delta_{DC}, \tag{54}$$

where a special notation is introduced:

$$(\mathbf{C} - \mathbf{P}_\tau)_{\alpha\beta\cdots\omega} = (\mathbf{C} - \mathbf{P}_\tau)_\alpha(\mathbf{C} - \mathbf{P}_\tau)_\beta \cdots (\mathbf{C} - \mathbf{P}_\tau)_\omega, \tag{55}$$

and $\alpha,\beta = x$, y, or z. In Eq. (54) $F_1(t_\tau), F_2(t_\tau)$, and $\lambda_{mn,1}, \lambda_{mn,2}$ are defined in Eqs. (40a) and (50), respectively.

The second term on the right-hand side of Eq. (53) may be evaluated by the property of the δ function:

$$\int_\Omega f(x)\delta(x - y)dx = f(y), \quad \text{if } y\in\Omega. \tag{56}$$

Thus it is not difficult to see that

$$\langle \chi_i(A)|\delta(\mathbf{r}_C)|\chi_j(B)\rangle = \frac{1}{4\pi}\sum_{mnkl}\lambda_{mn,1}W_\tau^{(ij)}e^{-t_\tau}. \quad (57)$$

Combining Eqs. (54) and (57) we have

$$[\langle \chi_i(A)|(\nabla_C\nabla_D V)|\chi_j(B)\rangle]_{\alpha\beta}$$

$$= -Z_C\sum_{mnkl}W_\tau^{(ij)}\{\lambda_{mn,2}F_2(t_\tau)(\mathbf{C}-\mathbf{P}_\tau)_{\alpha\beta}$$

$$-\lambda_{mn,1}[F_1(t_\tau)+\tfrac{1}{3}e^{-t_\tau}]\delta_{\alpha\beta}\}\delta_{DC}. \quad (58)$$

For the case $D=C=B\neq A$ the following relation is easily derived:

$$\nabla_B\nabla_B[\langle\chi_i(A)|V_B|\chi_j(B)\rangle] = -Z_B\sum_{mnkl}\lambda_{mn,0}W_\tau^{(ij)}\left\{[4b_n^2(\mathbf{B}_{nl}-\mathbf{P}_\tau)(\mathbf{B}_{nl}-\mathbf{P}_\tau)-2\sigma_{mn}]F_0(t_\tau)\right.$$

$$\left.-\left[-8a_mb_n(\mathbf{B}_{nl}-\mathbf{P}_\tau)(\mathbf{B}-\mathbf{P}_\tau)+\frac{2a_m^2}{a_m+b_n}\right]F_1(t_\tau)+4a_m^2(\mathbf{B}-\mathbf{P}_\tau)(\mathbf{B}-\mathbf{P}_\tau)F_2(t_\tau)\right\}, \quad (60)$$

$$\nabla_B[\langle\chi_i(A)|V_B\nabla_B|\chi_j(B)\rangle] = -Z_B\sum_{mnkl}\lambda_{mn,0}W_\tau^{(ij)}\{[4b_n^2(\mathbf{B}_{nl}-\mathbf{P}_\tau)(\mathbf{B}_{nl}-\mathbf{P}_\tau)-2\sigma_{mn}]F_0(t_\tau)$$

$$-[4b_n^2(\mathbf{B}_{nl}-\mathbf{P}_\tau)(\mathbf{B}-\mathbf{P}_\tau)-4a_mb_n(\mathbf{B}_{nl}-\mathbf{P}_\tau)(\mathbf{B}-\mathbf{P}_\tau)-2\sigma_{mn}]F_1(t_\tau)$$

$$-4a_mb_n(\mathbf{B}-\mathbf{P}_\tau)(\mathbf{B}-\mathbf{P}_\tau)F_2(t_\tau)\}, \quad (61)$$

$$\langle\chi_i(A)|V_B\nabla_B\nabla_B|\chi_j(B)\rangle = -Z_B\sum_{mnkl}\lambda_{mn,0}W_\tau^{(ij)}\left\{\left[4b_n^2(\mathbf{B}_{nl}-\mathbf{P}_\tau)(\mathbf{B}_{nl}-\mathbf{P}_\tau)+\frac{2b_n^2}{a_m+b_n}-2b_n\right]F_0(t_\tau)\right.$$

$$\left.-\left[8b_n^2(\mathbf{B}_{nl}-\mathbf{P}_\tau)(\mathbf{B}-\mathbf{P}_\tau)+\frac{2b_n^2}{a_m+b_n}\right]F_1(t_\tau)+4b_n^2(\mathbf{B}-\mathbf{P}_\tau)(\mathbf{B}-\mathbf{P}_\tau)F_2(t_\tau)\right\}. \quad (62)$$

Substituting Eqs. (57) and (60)–(62) into Eq. (59) and simplifying, we find the basis expectations in this case have the same form as Eq. (58). In the same way for $A=B=C=D$, we use the relation

$$[\langle\chi_i(A)|(\nabla_A\nabla_A V)|\chi_j(A)\rangle]_{\alpha\beta}$$

$$= [\langle\nabla_A\nabla_A\chi_i(A)|V_A|\chi_j(A)\rangle]_{\alpha\beta}$$

$$+ [\langle\chi_i(A)|V_A\nabla_A\nabla_A|\chi_j(A)\rangle]_{\alpha\beta}$$

$$+ 2[\langle\nabla_A\chi_i(A)|V_A\nabla_A|\chi_j(A)\rangle]_{\alpha\beta}$$

$$+ \frac{4\pi Z_C}{3}\langle\chi_i(A)|\delta(\mathbf{r}_A)|\chi_j(A)\rangle\delta_{\alpha\beta} \quad (63)$$

to show that Eq. (58) is also valid for this particular case.

C. $\langle\chi_i(A)|(\nabla_E\nabla_D\nabla_C V)|\chi_j(B)\rangle$ and $\langle\chi_i(A)|(\nabla_F\nabla_E\nabla_D\nabla_C V)|\chi_j(B)\rangle$

These are the third-rank tensor operator with 27 components and the fourth-rank tensor operator with 81 components, respectively.

$$[\langle\chi_i(A)|(\nabla_B\nabla_B V)|\chi_j(B)\rangle]_{\alpha\beta}$$

$$= [\langle\chi_i(A)|(\nabla_B\nabla_B V_B)|\chi_j(B)\rangle]_{\alpha\beta}$$

$$= [\nabla_B\nabla_B\langle\chi_i(A)|V_B|\chi_j(B)\rangle]_{\alpha\beta}$$

$$- 2[\nabla_B\langle\chi_i(A)|V_B\nabla_B|\chi_j(B)\rangle]_{\alpha\beta}$$

$$+ [\langle\chi_i(A)|V_B\nabla_B\nabla_B|\chi_j(B)\rangle]_{\alpha\beta}$$

$$+ \frac{4\pi Z_B}{3}\langle\chi_i(A)|\delta(\mathbf{r}_S)|\chi_j(B)\rangle\delta_{\alpha\beta}. \quad (59)$$

By a method similar to that for $\langle\chi_i(A)|(\nabla_C V)\chi_j(B)\rangle$, we have

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For these two operators the singularity at $\mathbf{r}_C$ produces the derivatives of the δ function. These terms can be evaluated by the property of the δ function:

$$\int_\Omega f(x)\delta'(x-y)dx = f'(y), \quad \text{if } y\in\Omega \quad (64)$$

and

$$\int_\Omega f(x)\delta''(x-y)dx = f''(y), \quad \text{if } y\in\Omega. \quad (65)$$

Then by essentially the same technique we have applied above, but one which is somewhat more tedious and complicated, the expectations for these two operators in the GLO basis are also obtained:

$$[\langle\chi_i(A)|(\nabla_E\nabla_D\nabla_C V)|\chi_j(B)\rangle]_{\alpha\beta\gamma}$$

$$= -Z_C\sum_{mnkl}W_\tau^{(ij)}\{\lambda_{mn,3}(\mathbf{C}-\mathbf{P}_\tau)_{\alpha\beta\gamma}F_3(t_\tau)$$

$$- \lambda_{mn,2}[F_2(t_\tau)+\tfrac{1}{3}e^{-t_\tau}][(\mathbf{C}-\mathbf{P}_\tau)_\alpha\delta_{\beta\gamma}$$

$$+ (\mathbf{C}-\mathbf{P}_\tau)_\beta\delta_{\alpha\gamma}+(\mathbf{C}-\mathbf{P}_\tau)_\gamma\delta_{\alpha\beta}]\}\delta_{EC}\delta_{DC}, \quad (66)$$

$$[\langle\chi_i(A)|(\nabla_F\nabla_E\nabla_D\nabla_C V)|\chi_j(B)\rangle]_{\alpha\beta\gamma\delta} = -Z_c\sum_{mnkl}W_\tau^{(ij)}\{\lambda_{mn,4}(\mathbf{C}-\mathbf{P}_\tau)_{\alpha\beta\gamma\delta}F_4(t_\tau)$$

$$-\lambda_{mn,3}[F_3(t_\tau)+\tfrac{1}{3}e^{-t_\tau}][(\mathbf{C}-\mathbf{P}_\tau)_{\alpha\beta}\delta_{\gamma\epsilon}+(\mathbf{C}-\mathbf{P}_\tau)_{\alpha\gamma}\delta_{\beta\epsilon}$$

$$+(\mathbf{C}-\mathbf{P}_\tau)_{\alpha\epsilon}\delta_{\beta\gamma}+(\mathbf{C}-\mathbf{P}_\tau)_{\beta\gamma}\delta_{\alpha\epsilon}+(\mathbf{C}-\mathbf{P}_\tau)_{\beta\epsilon}\delta_{\alpha\gamma}+(\mathbf{C}-\mathbf{P}_\tau)_{\gamma\epsilon}\delta_{\alpha\beta}]$$

$$+\lambda_{mn,2}[F_2(t_\tau)+\tfrac{1}{3}e^{-t_\tau}][\delta_{\alpha\beta}\delta_{\gamma\epsilon}+\delta_{\alpha\gamma}\delta_{\beta\epsilon}+\delta_{\alpha\epsilon}\delta_{\beta\gamma}]\}\delta_{FC}\delta_{EC}\delta_{DC}, \quad (67)$$

disregarding the relationship between C, A, and B.

D. $\langle\chi_i(A)|\nabla_C|\chi_j(B)\rangle$, $\langle\chi_i(A)|\nabla_D\nabla_C|\chi_j(B)\rangle$ and $\langle\nabla_D\chi_i(A)|\nabla_C\chi_j(B)\rangle$

The operator ∇_C is a vector operator, the other two are the second-rank tensor operators with nine components. From Eq. (12) it is easy to get

$$\nabla_C|\chi_j(B)\rangle$$

$$= \sum_{nl}(-1)^l 2d_{jn}N_n b_n(\mathbf{B}_{nl} - \mathbf{r})\exp(-b_n r^2_{B_{nl}})\delta_{CB},$$

(68)

and

$$[\nabla_D\nabla_C|\chi_j(B)\rangle]_{\alpha\beta}$$

$$= \sum_{nl}(-1)^l d_{jn}N_n[2b_n\delta_{\alpha\beta}$$

$$- 4b^2_n(\mathbf{B}_{nl} - \mathbf{r})_{\alpha\beta}]\exp(-b_n r^2_{B_{nl}})\delta_{DC}\delta_{CB}.$$

(69)

With these expressions the basis expectations can be obtained:

$$\langle\chi_i(A)|\nabla_C|\chi_j(B)\rangle = -\sum_{mnkl} 2\sigma_{mn}W^{(ij)}_\tau(\mathbf{A}_{mk} - \mathbf{B}_{nl})\delta_{CB},$$

(70)

$$[\langle\chi_i(A)|\nabla_D\nabla_C|\chi_j(B)\rangle]_{\alpha\beta}$$

$$= \sum_{mnkl} 2\sigma_{mn}W^{(ij)}_\tau[2\sigma_{mn}(\mathbf{A}_{mk} - \mathbf{B}_{nl})_{\alpha\beta} - \delta_{\alpha\beta}]\delta_{DB}\delta_{CB}$$

(71)

and

$$[\langle\nabla_D\chi_i(A)|\nabla_C\chi_j(B)\rangle]_{\alpha\beta}$$

$$= -\sum_{mnkl} 2\sigma_{mn}W^{(ij)}_\tau[2\sigma_{mn}(\mathbf{A}_{mk} - \mathbf{B}_{nl})_{\alpha\beta}$$

$$- \delta_{\alpha\beta}]\delta_{DA}\delta_{CB}.$$

(72)

It is worth noticing that in Eqs. (71) and (72) the coordinates of nucleus C appear only in δ symbols. This is helpful in programming.

E. $\langle\chi_i(A)|\nabla|\chi_j(B)\rangle$

Here the gradient is taken with respect to electronic coordinates. The formula for this expectation is the same as Eq. (70) except for the sign:

$$\langle\chi_i(A)|\nabla|\chi_j(B)\rangle = 2\sum_{mnkl} \sigma_{mn}W^{(ij)}_\tau(\mathbf{A}_{mk} - \mathbf{B}_{nl}).$$

(73)

V. APPLICATIONS

As described in Sec. I, these operators can be applied to a variety of problems. With the GLO as basis functions and based on the Whitten SCF/CI programs, we have revised the SCF/CI programs to include the expectations of the above operators and those for the Born correction, Born couplings, etc. In this section we give just a few examples of the calculations. Further applications will be reported elsewhere.[38]

A. The orbital stress for N_2

The orbital stress was shown to be an important property of molecular orbitals, and the transition stress, which is the difference between the orbital stress for an upper molecular orbital and the one for a lower molecular orbital, was demonstrated to be one of the fundamental properties of electronic states.[28,29] However, it is hard to obtain practically useful numerical values for orbital stress because of the so-called *Hellmann–Feynman error*.[16] Therefore, in previous work the orbital stresses were obtained from Hartree–Fock accuracy wave functions.[33] Here we give the *ab initio* results for the orbital stress of N_2 (see Table I) by using Eq. (49) and various basis sets. The last column in Table I is the net stress:

$$S_{\text{net}} = \frac{Z_A Z_B}{R^2_0} + \sum_j \lambda_j s_j,$$

(74)

where R_0 is the equilibrium bond length of the ground state, λ_j is the occupation number in the jth molecular orbital, and s_j is the orbital stress of this molecular orbital. Theoretically, the net stress should be equal to zero. Table I demonstrates that poor basis sets give larger net stress and better basis sets give smaller net stress, as would be expected. The calculated values demonstrate that the so-called *hard polarized basis*[16] effectively improves the calculated results for orbital stress. A hard p-type GLO evidently increases the orbital stress for the two core orbitals and a relatively hard d-type GLO strongly improves the evaluation for the orbital stress of the

TABLE I. *Ab initio* calculation of orbital stress for N_2.[a]

Basis	Source of w/s	E_{SCF}	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	Net stress[f]
STO $2s1p$	Ref. 34	−108.6336	−0.876	−0.919	−2.137	0.522	−0.704	0.217	1.950
GLO $[3s2p]$[32]	This work	−108.8780	−0.876	−0.862	−2.186	0.418	−0.739	0.133	1.757
GLO $[3s3p]$[b]	This work	−108.8793	−1.016	−0.988	−2.151	0.376	−0.738	0.118	1.182
GLO $[3s2p1d]$[c]	This work	−108.9584	−0.861	−0.852	−2.263	0.401	−0.965	−0.031	0.387
GLO $[3s3p1d]$[d]	This work	−108.9597	−0.941	−0.917	−2.209	0.384	−0.964	−0.050	0.135
STO $[5s3p3d\,1f\,]$[e]	Ref. 33	−108.9928	−0.949	−0.890	−2.175	0.382	−0.997	−0.125	−0.048

[a] All numbers are in a.u.
[b] $[3s2p]$ plus one p basis with $\zeta = 10.0$.
[c] $[3s2p]$ plus one d basis with $\zeta = 1.10$.
[d] $[3s2p]$ plus one p basis with $\zeta = 10.0$ and one d basis with $\zeta = 1.10$.
[e] This result has achieved true Hartree–Fock accuracy.
[f] Accuracy and consistency of the numerical results are measured by smallness of the net stress (see the text).

TABLE II. The Born correction for regular states and the avoided crossing states of N_2.[a]

Items	States	Nuclear separation (a.u.)
		1.800	2.000	2.0680	2.100	2.300	2.400	2.500	2.540	2.560	2.580	2.590	2.600	2.620	2.650	2.700	2.800	3.000
h_1^z	$X\,^1\Sigma_g^+$	147.6	147.6	147.5	147.5	147.8	147.7	147.4	147.4	147.3	147.3	147.3	147.3	147.3	147.4	147.4	147.6	148.0
	$^1\Sigma_g^+\,(II)$	142.3	143.8	143.6	143.5	144.7	145.2	145.6	145.7	145.7	145.8	145.9	145.9	146.0	146.0	146.2	146.5	146.0
	$C,C'\,^3\Pi_u$	146.2	145.8	145.6	145.9	148.0	155.6	236.4	399.9	577.6	723.2	755.9	685.0	505.4	275.9	173.1	151.8	147.6
	$^3\Pi_u\,(II)$	146.9	146.2	146.3	146.6	148.0	154.3	231.5	394.8	574.7	725.7	765.9	701.1	542.1	364.4	505.7	303.0	149.0
$h_1^y = h_1^z$	$X\,^1\Sigma_g^+$	142.8	142.9	143.0	143.0	143.5	143.7	143.9	144.0	144.1	144.1	144.1	144.2	144.2	144.3	144.4	144.6	144.9
	$^1\Sigma_g^+\,(II)$	147.8	146.0	146.8	146.7	146.4	146.3	146.3	146.3	146.3	146.3	146.3	146.3	146.3	146.3	146.3	146.3	146.3
	$C,C'\,^3\Pi_u$	142.8	143.1	143.0	142.9	143.1	143.2	143.5	143.8	144.1	144.4	144.6	144.9	145.1	145.4	145.5	145.6	145.6
	$^3\Pi_u\,(II)$	145.2	146.2	146.0	145.8	145.6	145.4	145.4	145.2	145.0	144.7	144.5	144.3	144.2	144.1	144.4	145.1	145.3
$h_2 + h_3$	$X\,^1\Sigma_g^+$	501.4	495.6	494.5	493.5	490.7	489.6	489.0	488.7	488.7	488.7	488.5	488.3	488.2	488.0	487.8	487.3	486.6
	$^1\Sigma_g^+\,(II)$	511.5	507.1	506.2	505.4	501.8	500.3	498.9	498.4	498.2	498.0	497.0	497.7	497.5	497.2	496.7	495.7	494.0
	$C,C'\,^3\Pi_u$	507.9	502.7	500.8	499.1	495.7	494.2	493.1	493.0	493.0	493.0	493.0	493.0	492.9	492.6	492.1	490.5	488.3
	$^3\Pi_u\,(II)$	507.3	503.2	501.4	500.0	496.4	494.6	493.4	492.4	492.3	492.0	491.8	491.7	491.4	491.1	490.8	489.8	488.3
h	$X\,^1\Sigma_g^+$	934.6	929.0	928.0	927.0	925.5	924.7	924.2	924.1	924.2	924.2	924.0	924.0	923.9	924.0	924.0	924.1	924.4
	$^1\Sigma_g^+\,(II)$	949.4	944.7	943.5	942.3	939.3	938.1	937.1	936.7	936.5	936.4	936.3	936.2	936.1	935.8	935.5	934.8	933.5
	$C,C'\,^3\Pi_u$	939.7	934.7	932.4	930.8	929.9	936.2	1016.5	1180.5	1358.8	1505.0	1538.1	1467.8	1288.5	1059.3	956.2	933.5	927.1
	$^3\Pi_u\,(II)$	944.6	941.8	939.7	938.2	935.6	939.7	1015.7	1177.6	1357.0	1507.1	1546.7	1481.4	1321.9	1143.7	1285.3	1083.0	927.9

[a] All data for the Born correction are in cm^{-1}.

$1\pi_u$ orbital. These calculated orbital stresses from a $[3s2p]$ basis set[32] plus one hard p function and one d function are in good agreement with the values obtained earlier[29] from the Hartree–Fock accuracy wave functions.[33]

B. The Born correction for N_2

The Born corrections allow more accurate calculation of potential-energy surfaces. The Born corrections have been calculated for a few electronic states of H_2 and several other molecules.[4–12] For a BO electronic state Ψ_i of the diatomic molecule AB, the Born correction is a sum of three parts[10]:

$$h = h_1 + h_2 + h_3, \tag{75}$$

where

$$h_1 = -\frac{1}{2\mu} \langle \Psi_i | \nabla_R^2 | \Psi_i \rangle, \tag{76}$$

$$h_2 = -\frac{1}{2M} \langle \Psi_i | \sum_i \nabla_i^2 | \Psi_i \rangle, \tag{77}$$

$$h_3 = -\frac{1}{M} \langle \Psi_i | \sum_{i\neq j} \nabla_i \cdot \nabla_j | \Psi_i \rangle, \tag{78}$$

and μ is the reduced mass of the two nuclei and M is the sum of masses for the nuclei A and B. The h_1 defined in Eq. (76) is the sum of three terms:

$$h_1 = h_1^x + h_1^y + h_1^z, \tag{79}$$

where

$$h_1^x = -\frac{1}{2\mu} \langle \Psi_i | \frac{\partial^2}{\partial X^2} | \Psi_i \rangle, \quad h_1^y = -\frac{1}{2\mu} \langle \Psi_i | \frac{\partial^2}{\partial Y^2} | \Psi_i \rangle,$$

$$h_1^z = -\frac{1}{2\mu} \langle \Psi_i | \frac{\partial^2}{\partial Z^2} | \Psi_i \rangle, \tag{80}$$

and $X = X_B - X_A$, $Y = Y_B - Y_A$, $Z = Z_B - Z_A$ are the relative nuclear coordinates.

The calculation of h_1 will be discussed in detail later. The term h_2 actually is the electronic kinetic energy divided by a constant. The term h_3 can be evaluated by means of Eq. (73).

Using the $[3s3p1d]$ basis which is the widely used $[3s2p]$ basis[32] augmented by a p function and a d function (see footnote c in Table I), we carried out the calculations of the Born corrections for $X\,^1\Sigma_g^+$, $^1\Sigma_g^+\,(II)$, $C,C'\,^3\Pi_u$, and

TABLE III. The comparison of two methods to calculate the Born correction.[a]

Items	States	Methods	Nuclear separation (a.u.)
			1.80	2.00	2.20	2.40	2.60	2.80	3.00
h_1^x	$X\,^1\Sigma_g^+$	A	146.6	147.2	147.9	148.7	148.5	147.7	147.4
	$X\,^1\Sigma_g^+$	B	147.6	147.6	147.7	147.7	147.3	147.6	148.0
	$C,C'\,^3\Pi_u$	A	145.2	145.3	146.5	156.4	689.8	151.7	146.7
	$C,C'\,^3\Pi_u$	B	146.2	145.3	146.4	155.6	685.0	151.8	147.6
$h_1^y = h_1^z$	$X\,^1\Sigma_g^+$	A	143.3	142.2	143.6	144.2	144.5	144.6	144.8
	$X\,^1\Sigma_g^+$	B	142.8	142.9	143.3	143.7	144.2	144.6	144.9
	$C,C'\,^3\Pi_u$	A	143.2	143.2	143.2	143.8	144.9	145.2	145.0
	$C,C''\,^3\Pi_u$	B	142.8	143.1	143.0	143.2	144.9	145.6	145.6

[a] All numbers for the Born correction are in cm^{-1}.

$^3\Pi_u$ (*II*) for N_2 at several nuclear separations. The results are shown in Table II.

1. The comparison of two numerical methods

As is easily seen, the term h_2 actually is the electronic kinetic energy divided by a constant. The term h_3 can be evaluated simply by means of Eq. (73). However, the calculation for h_1 is the central point for the Born coupling calculation. It can be calculated by either Eqs. (16), (18), (20), (22), (25), and (71) or Eqs. (17), (19), (21), (23), (26), and (72), namely based on operator (6) or (7). We will call the former method A and the latter method B, respectively. Method B, proposed first by Sellers and Pulay,[7,8] has two evident advantages. First, it requires less computer time for the present calculation. Method A requires five full calculations of the electronic wave functions (i.e., at Q_0, $Q_0 + \Delta X$, $Q_0 + 2\Delta X$, $Q_0 + \Delta Y$, and $Q_0 + 2\Delta Y$, respectively) if the equivalence of h_1^y and h_1^z is used, while method B requires only three such calculations. Second, converged results are easy to obtain by method B and the calculated values are reasonably stable in a wide range of ΔX, etc., since only the first derivatives of CI and MO coefficients are involved, while for method A there is only a rather narrow region which gives the stable results. To search this narrow stable region also takes much computer time.

The better method is therefore method B, unless a simultaneous calculation of the Born couplings and the Born corrections is required. However, the calculated values by method B, that have been reported so far, are much lower than those from other methods. The only available quantitative comparison is for the Born correction for the ground state of the hydrogen molecule. Method B gives only about one quarter[8] of the accurate values obtained by Kolos and Wolniewicz.[4] Thus, the practical reliability of method B, though there is no problem theoretically, must be demonstrated.

Our program with the GLO as basis demonstrates that these two methods are practically equivalent. The calculated results for the Born couplings for the ground states and lower electronic excited states of hydrogen molecules with both method A and method B are in good agreement with the previous accurate values.[38] In this work, the calculation of the Born corrections for the ground state and several electronic excited states, including the state $C,C'\,^3\Pi_u$, an avoided crossing state, again shows the equivalence of these methods. As an example, Table III shows the Born corrections for the ground state $X\,^1\Sigma_g^+$ and the avoided crossing valence state $C,C'\,^3\Pi_u$. These data demonstrate that the coincidence of results for these two methods is about 99%. Thus we have shown that method B, based on operator (6), is an economical and practical method for the calculation of the Born corrections. The role of operator (6) in the calculation of the Born couplings is discussed elsewhere.[38]

2. The Born correction of the avoided crossing states

The electronic states $X\,^1\Sigma_g^+$ and $^1\Sigma_g^+$ (*II*) are "regular" states, i.e., far away from crossings or avoided crossings. The values of the Born correction for these states are very slowly varying. In a large region of nuclear separations these values

remain almost constant. On the other hand, the electronic state $C,C'\,^3\Pi_u$ is a double-well state (see Ref. 39). Its first well is designated $C\,^3\Pi_u$ with $2\sigma_u^1 1\pi_u^4 3\sigma_g^2 1\pi_u^1$ as its main electronic configuration; the second well, which is very shallow, is denoted by $C'\,^3\Pi_u$ with $2\sigma_u^2 1\pi_u^3 3\sigma_g^1 1\pi_u^2$ as the main electronic configuration. An unobserved $^3\Pi_u$ (*II*) state[39] is located above this double well state $C,C'\,^3\Pi_u$. There is an avoided crossing between these two states, $^3\Pi_u$ (*II*) and $C,C'\,^3\Pi_u$.

The values obtained (see Table II and Fig. 1) for these states show that Born corrections of the states involved in an avoided crossing peak sharply near the avoided crossing region, as shown in Fig. 1. Meanwhile, the values of the Born correction for $^3\Pi_u$ (*II*) (see the last row in Table II) shows that there are two peaks. The first one originates from the avoided crossing with $C,C'\,^3\Pi_u$ and the second one is caused by the interaction with other unobserved states.[39]

The data in Table II also shows that this variance, compared with the regular states, is mainly caused by the h_1^x term.

3. Contribution analysis

Both Eqs. (16) and (17) have three terms. Among them the first term is the contribution from a variety of CI coefficients, called *the CI contribution*. The last term reflects the effects of nuclear displacement on Slater determinants, namely on molecular orbitals, so that it may be called *the*
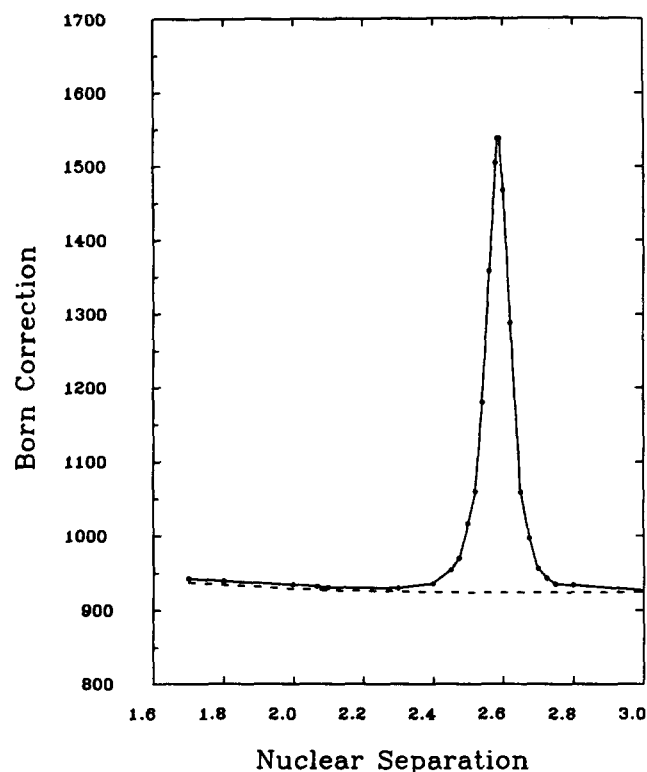

FIG. 1. The Born correction for $X\,^1\Sigma_g^+$ and $C,C'\,^3\Pi_u$ states (in cm^{-1}) vs nuclear separation (in a.u.) for N_2. Dash line: for $X\,^1\Sigma_g^+$; full line for $C,C'\,^3\Pi_u$, a sharp peak appears near the avoided crossing with $^3\Pi_u$ (*II*).

TABLE IV. The contribution analysis in the Born correction.

States	Nuclear separation a.u.	Items	Contributions %	Items	Contributions %
$X\,^1\Sigma_g^+$	2.068	CI, in h_1^x	0.22	Ci, in h_1^y	0.00
		MO, in h_1^x	99.94	MO, in h_1^y	100.00
		mixed, in h_1^x	-0.16	mixed, in h_1^y	0.00
	2.590	CI, in h_1^x	0.52	Ci, in h_1^y	0.00
		MO, in h_1^x	100.48	MO, in h_1^y	100.00
		mixed, in h_1^x	-1.00	mixed, in h_1^y	0.00
$C,C'\,^3\Pi_u$	2.068	CI, in h_1^x	0.63	CI, in h_1^y	0.00
		MO, in h_1^x	100.18	MO, in h_1^y	100.00
		mixed, in h_1^x	-0.81	mixed, in h_1^y	0.00
	2.590	CI, in h_1^x	80.38	CI, in h_1^y	0.00
		MO, in h_1^x	19.49	MO, in h_1^y	100.00
		mixed, in h_1^x	0.10	mixed, in h_1^y	0.00

MO contribution. The second term, which depends upon both, is called *the mixed contribution.*

Table IV shows the contribution analysis of the Born correction near the avoided crossing region and far away from this region. It is demonstrated that the strong variance of the Born correction for the states involved in an avoided crossing is mainly contributed by configuration interaction.

These results and other work to be reported elsewhere[38] demonstrate that the GLO approach is very effective for reliable calculations of the Born correction, the Born coupling, and related quantities.

[1]M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927).

[2]M. Born and K. H. Huang, *Dynamical Treatment of Crystal Lattices* (Clarendon, Oxford, 1954).

[3]Y. Zhang and R. N. Porter, J. Chem. Phys. **88**, 4949 (1988).

[4]W. Kolos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964).

[5]D. M. Bishop and R. W. Wetmore, Mol. Phys. **26**, 145 (1973).

[6]M. Peric, S. D. Peyerimhoff, and R. J. Buenker, Mol. Phys. **49**, 379 (1983).

[7]H. Sellers and P. Pulay, Chem. Phys. Lett. **103**, 463 (1984).

[8]H. Sellers, Chem. Phys. Lett. **108**, 339 (1984).

[9]N. C. Handy, Y. Yamaguchi, and H. F. Schaefer III, J. Chem. Phys. **84**, 4481 (1986).

[10]K. Dressler and L. Wolniewicz, J. Chem. Phys. **85**, 2821 (1986).

[11]B. C. Garrett and D. G. Truhlar, J. Chem. Phys. **82**, 4543 (1985).

[12]N. Sukumar, Ph.D. dissertation, State University of New York at Stony Brook, 1984.

[13]A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blais, J. Chem. Phys. **86**, 6258 (1987).

[14]L. T. Redmon, Phys. Rev. A **25**, 2453 (1982).

[15]B. H. Lengsfield III and D. R. Yarkony, J. Chem. Phys. **84**, 348 (1986).

[16]P. Habitz and C. Votava, J. Chem. Phys. **72**, 5532 (1980).

[17]R. Cimiraglia, M. Persico, and J. Tomasi, Chem. Phys. **53**, 357 (1980).

[18]G. Hirsch, P. J. Bruna, R. J. Buenker, and S. D. Peyerimhoff, Chem. Phys. **45**, 335 (1980).

[19]S. E. Butler, Phys. Rev. A **23**, 23 (1981).

[20]B. R. Johnson and R. D. Levine, Chem. Phys. Lett. **13**, 168 (1972).

[21]J. F. Gaw, Y. Yamaguchi, H. F. Schaefer III, and N. C. Handy, J. Chem. Phys. **85**, 5132 (1986).

[22]R. J. Buenker, G. Hirch, S. D. Peyerimhoff, P. J. Bruna, and C. Petrongolo, Stud. Phys. Theor. Chem. **21**, 81 (1982).

[23]H. Preuss, Z. Naturforsch. Teil A **11**, 823 (1956).

[24]J. L. Whitten, J. Chem. Phys. **39**, 349 (1963); **44**, 359 (1969).

[25]J. D. Petke, J. L. Whitten, and A. W. Douglas, J. Chem. Phys. **51**, 256 (1969).

[26]See, for example, H. Le Rouzo and B. Silvi, Int. J. Quantum Chem. **13**, 297, 311, 325 (1978), and references therein.

[27]M. S. Child, *Molecular Collision Theory* (Academic, New York, 1974).

[28]Y. Zhang and D. M. Hanson, Chem. Phys. Lett. **127**, 33 (1986).

[29]Y. Zhang and D. M. Hanson, J. Chem. Phys. **86**, 347; 666 (1987).

[30]P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, J. Am. Chem. Soc. **101**, 2550 (1979).

[31]Y. Zhang, Ph. D. dissertation, State University of New York at Stony Brook, 1987.

[32]T. H. Dunning, Jr. and P. J. Hay, in *Method of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1976).

[33]P. E. Cade and A. C. Wahl, At. Data Nucl. Data Tables **13**, 339 (1974).

[34]B. J. Ransil, Rev. Mod. Phys. **32**, 245 (1960).

[35]S. F. Boys, Proc. R. Soc. London Ser. A **200**, 542 (1950); **258**, 402 (1960).

[36]I. Shavitt, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1963), Vol. 2.

[37]A. Tang, Z. Yang, and Q. Li, *Quantum Chemistry* (Science, Beijing, 1982).

[38]Y. Zhang and R. N. Porter (in preparation).

[39]H. H. Michels, in *The Excited State in Chemical Physics Part* 2, edited by J. Wm. McGowan, Advances in Chemical Physics Vol. XLV, edited by I. Prigogine and S. Rice (Wiley Interscience, New York, 1981), p. 255.