

A METHOD FOR DESCRIBING RESONANCE BETWEEN GENERALIZED VALENCE BOND WAVEFUNCTIONS

Arthur F. VOTER and William A. GODDARD III

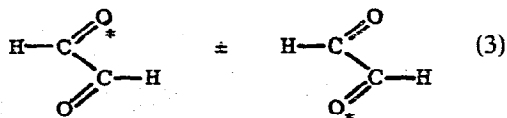
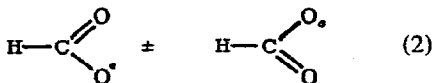
Arthur Amos Noyes Laboratory of Chemical Physics*, California Institute of Technology, Pasadena, California 91125, USA

Received 8 December 1980

In a valence bond (VB) description of wavefunctions there may be several distinct but energetically similar bonding structures. Examples include aromatic molecules (e.g. benzene) and excited states of molecules with equivalent chromophores (e.g. glyoxal). The variational generalization of VB theory, the generalized valence bond (GVB) method, has limitations for such systems since it can only describe one of the bonding structures, allowing no explicit mixing or "resonance" with the other structures. We present herein a method for evaluating the matrix elements necessary to optimize the mixing between the various distinct bonding structures. Evaluation of such matrix elements has heretofore been computationally difficult since the wavefunctions in general have nonzero overlap. Applications of the method are presented for the resonance in allyl radical and the splitting of the localized core hole states of N_2^+ .

1. Introduction

For many molecules the natural approach to studying the electronic wavefunction is to superimpose the wavefunctions for various bonding structures. For example,



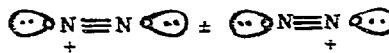
Unfortunately the wavefunctions for different bonding structures are generally nonorthogonal, leading to severe difficulties in evaluating the energy and in optimizing the orbitals. These difficulties become even more severe when electron correlation effects are included.

* Contribution No. 6355.

In this paper we describe an approach for calculating the interaction of nonorthogonal correlated wavefunctions that does not suffer from the usual computational dependence. In addition, we report applications of this approach to two typical problems:

(a) The resonance of the two equivalent configurations of allyl (1) where each π bond is correlated (GVB level).

(b) The resonance of the 1s core ionization states of N_2



where the core hole is allowed to be localized on one N atom, and the remainder of the molecule is fully correlated (GVB level).

2. The method

Consider a state Ψ involving the superposition of two wavefunctions Ψ^A and Ψ^B ,

$$\Psi = C_A \Psi^A + C_B \Psi^B, \quad (4)$$

where Ψ^A and Ψ^B are correlated (multi-configurational) wavefunctions for two possible bonding structures. [For simplicity we consider only two configurations in (4); the generalization to multiple terms is trivial.] Each correlated wavefunction Ψ^A and Ψ^B can be expanded in terms of determinantal wavefunctions $\{\psi_i^A\}$ as

$$\Psi^A = \sum_i C_i^A \psi_i^A, \quad (5)$$

where

$$\psi_i^A = \mathcal{A} \left[\left(\prod_j \phi_j^{iA} \right) \chi_i^A \right]. \quad (6)$$

Assuming that Ψ^A and Ψ^B are normalized, the energy of the wavefunction Ψ is

$$E = \frac{C_A^2 E_A + C_B^2 E_B + 2C_A C_B H_{AB}}{C_A^2 + C_B^2 + 2C_A C_B S_{AB}}, \quad (7)$$

where E_A and E_B are the energies of Ψ^A and Ψ^B , respectively, and

$$S_{AB} = \langle \Psi^A | \Psi^B \rangle = \sum_i \sum_j C_i^A C_j^B \langle \psi_i^A | \psi_j^B \rangle, \quad (8)$$

$$H_{AB} = \langle \Psi^A | \mathcal{H} | \Psi^B \rangle = \sum_i \sum_j C_i^A C_j^B \langle \psi_i^A | \mathcal{H} | \psi_j^B \rangle. \quad (9)$$

Because of the nonorthogonality of the orbitals

$$\{\phi_k^{iA} : k = 1, \dots, M\} \quad (10)$$

with

$$\{\phi_k^{iB} : k = 1, \dots, M\} \quad (11)$$

the evaluation of terms like $\langle \psi_i^A | \psi_j^B \rangle$ and $\langle \psi_i^A | \mathcal{H} | \psi_j^B \rangle$ would normally involve tedious computation of numerous minors and subminors of the determinant of the overlaps between the A and B sets of orbitals.

The determinantal wavefunctions ψ_i^A and ψ_j^B are invariant (to within a phase) under unitary transformations \hat{U}^{iA} and \hat{U}^{jB} of the orbitals

$$\bar{\phi}_i^{iA} = \sum_k \phi_k^{iA} U_{ki}^{iA}, \quad \bar{\phi}_j^{jB} = \sum_k \phi_k^{jB} U_{kj}^{jB}. \quad (12)$$

Thus, by choosing these transformations so that the new orbitals are biorthogonal [1]

$$\langle \bar{\phi}_k^{iA} | \bar{\phi}_l^{jB} \rangle = \lambda_k \delta_{kl}, \quad (13)$$

we can greatly simplify evaluation of matrix elements such as $\langle \psi_i^A | \mathcal{H} | \psi_j^B \rangle$ and $\langle \psi_i^A | \psi_j^B \rangle$. For a

closed-shell configuration (only doubly-occupied orbitals) the same transformations are applied to the α -spin and β -spin orbitals, leading to

$$\langle \psi_i^A | \psi_j^B \rangle = \lambda_1^2 \lambda_2^2, \dots, \lambda_n^2, \quad (14)$$

$$\begin{aligned} \langle \psi_i^A | \mathcal{H} | \psi_j^B \rangle &= 2 \sum_k \eta_k \langle \bar{\phi}_k^A | h | \bar{\phi}_k^B \rangle \\ &+ \sum_{k,l} \eta_{kl} [2 \langle \bar{\phi}_k^A \bar{\phi}_k^B | \bar{\phi}_l^A \bar{\phi}_l^B \rangle - \langle \bar{\phi}_k^A \bar{\phi}_l^B | \bar{\phi}_l^A \bar{\phi}_k^B \rangle] \end{aligned} \quad (15)$$

(where $\bar{\phi}^{iA}$ and $\bar{\phi}^{jB}$ have been denoted simply as $\bar{\phi}^A$ and $\bar{\phi}^B$) and

$$\langle \phi_i \phi_j | \phi_k \phi_l \rangle = \int d^3 r_1 \int d^3 r_2 \phi_i^*(1) \phi_j(1) \phi_k^*(2) \phi_l(2) \quad (16)$$

and

$$\eta_k = (\lambda_1^2 \lambda_2^2 \dots \lambda_n^2) / \lambda_k, \quad \eta_{kl} = (\lambda_1^2 \lambda_2^2 \dots \lambda_n^2) / \lambda_k \lambda_l. \quad (17)$$

For a more general wavefunction in which the determinants are not closed-shell, the transformations factor into a transformation among α spin orbitals and a different transformation among β spin orbitals (taking care that the transformation does not change the phase). The result in this case is

$$\langle \psi_i^A | \psi_j^B \rangle = \lambda_{1a} \lambda_{2a} \dots \lambda_{na} \lambda_{1b} \lambda_{2b} \dots \lambda_{mb}, \quad (18)$$

$$\begin{aligned} \langle \psi_i^A | \mathcal{H} | \psi_j^B \rangle &= \sum_{ka} \eta_{ka} \langle \bar{\phi}_{ka}^A | h | \bar{\phi}_{ka}^B \rangle + \sum_{kb} \eta_{kb} \langle \bar{\phi}_{kb}^A | h | \bar{\phi}_{kb}^B \rangle \\ &+ \sum_{ka > la} \eta_{ka,la} [\langle \bar{\phi}_{ka}^A \bar{\phi}_{ka}^B | \bar{\phi}_{la}^A \bar{\phi}_{la}^B \rangle \\ &\quad - \langle \bar{\phi}_{ka}^A \bar{\phi}_{la}^B | \bar{\phi}_{la}^A \bar{\phi}_{ka}^B \rangle] \\ &+ \sum_{kb > lb} \eta_{kb,lb} [\langle \bar{\phi}_{kb}^A \bar{\phi}_{kb}^B | \bar{\phi}_{lb}^A \bar{\phi}_{lb}^B \rangle - \langle \bar{\phi}_{kb}^A \bar{\phi}_{lb}^B | \bar{\phi}_{lb}^A \bar{\phi}_{kb}^B \rangle] \\ &+ \sum_{ka,lb} \eta_{ka,lb} \langle \bar{\phi}_{ka}^{iA} \bar{\phi}_{ka}^{jB} | \bar{\phi}_{lb}^{iA} \bar{\phi}_{lb}^{jB} \rangle, \end{aligned} \quad (19)$$

where ka, la indicate orbitals corresponding to α spin, kb, lb indicate orbitals corresponding to β spin

$$\eta_{ka} = \langle \psi_i^A | \psi_j^B \rangle \lambda_{ka} \quad (20a)$$

and

$$\eta_{ka,lb} = \langle \psi_i^A | \psi_j^B \rangle / \lambda_{ka} \lambda_{lb}. \quad (20b)$$

Thus the S_{AB} and H_{AB} of eqs. (8) and (9) can be evaluated by applying the above formulae to each pair of determinants (for an open-shell system, this requires four separate transformations to biorthogonal orbitals). For a GVB wavefunction in which each of n bonds is correlated with two natural orbitals, the resulting GVB($n/2n$)-PP wavefunction can be written as

$$\mathcal{A}\{[\text{core}][C_{a1}\phi_{a1}^2 + C_{b1}\phi_{b1}^2][C_{a2}\phi_{a2}^2 + C_{b2}\phi_{b2}^2]\dots \\ \dots [C_{an}\phi_{an}^2 + C_{bn}\phi_{bn}^2]\}, \quad (21)$$

leading to 2^n determinants. [This leads to the evaluation of 2^{2n} terms of the form (8) and (9).] The approach can, of course, be applied to find H_{AB} between any two multiconfigurational wavefunctions.

Wavefunctions obtained by this procedure are referred to as resonating generalized valence bond or R-GVB.

The computational time required for the allyl case (13 orbitals per wavefunction, four determinant pairs) was 105 s of CPU on a VAX 11/780, to be compared with 1300 s required to calculate the integrals over 37 gaussian basis functions and 936 s to converge the GVB 1/2 wavefunction (19 iterations).

3. Allyl radical

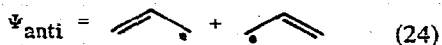
There are two bonding structures for allyl radical ($\text{H}_2\text{C}-\text{CH}-\text{CH}_2$), namely,



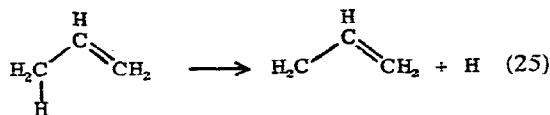
That is, the π bond can be on the left or right, and the π radical orbital is on the opposite center. These wavefunctions can be combined into a resonance (stabilized) form



and an antiresonance (destabilized) form



The experimental consequence of this resonance stabilization is that the CH bond energy of propene



is 87 kcal [2], whereas a terminal CH bond for an alkane would normally be 98 kcal [2]. This difference, 11 kcal, is generally referred to as the resonance energy. It need not be identical to the resonance stabilization of (23) for reasons discussed later in this section.

The wavefunctions for the bonding structures in (22) are

$$\psi_\ell = \mathcal{A}\{[\sigma_\ell](\phi_\ell\phi_c + \phi_c\phi_\ell)\phi_r\alpha\beta\alpha\}$$

and (26)

$$\psi_r = \mathcal{A}\{[\sigma_r](\phi_r\phi_c + \phi_c\phi_r)\phi_\ell\alpha\beta\alpha\}$$

(where only the π electrons are written explicitly), each containing a two-electron π bond to the central atom. Optimizing the orbitals of ψ_ℓ and ψ_r leads to π orbitals ϕ_ℓ , ϕ_c , and ϕ_r that are different between ψ_ℓ and ψ_r . Fig. 1 shows the π orbitals for ψ_ℓ . The energies for the resonant and antiresonant states are given by

$$E_{\text{res}} = (H_{\ell\ell} - H_{r\ell}) / (1 - S_{\ell r}) = H_{\ell\ell} - \epsilon_r, \\ E_{\text{anti}} = (H_{\ell\ell} + H_{r\ell}) / (1 + S_{\ell r}) = H_{\ell\ell} + \epsilon_a, \quad (27)$$

where

$$H_{\ell\ell} = H_{rr} = \langle \psi_\ell | \mathcal{H} | \psi_\ell \rangle, \quad S_{\ell r} = \langle \psi_\ell | \psi_r \rangle, \\ H_{r\ell} = \langle \psi_r | \mathcal{H} | \psi_\ell \rangle \quad (28)$$

and the resonance energy ϵ_r and antiresonant energy ϵ_a are defined. Note that the σ orbitals of ψ_ℓ and ψ_r are also slightly different, an effect that is included in these calculations.

The results are in table 1. Mixing the GVB wavefunctions ψ_ℓ and ψ_r yields $S_{\ell r} = -0.754$ and $H_{r\ell} = 87.763$ hartree, leading to a resonance energy $\epsilon_r = 9.8$ kcal. This resonance energy does not correspond exactly to the experimental value for three reasons. First, the experimental resonance energy is obtained by comparing two bonds with different steric interactions. Second, the experimental resonance energy includes the energy required to change the geometry from one long carbon-carbon single bond and one

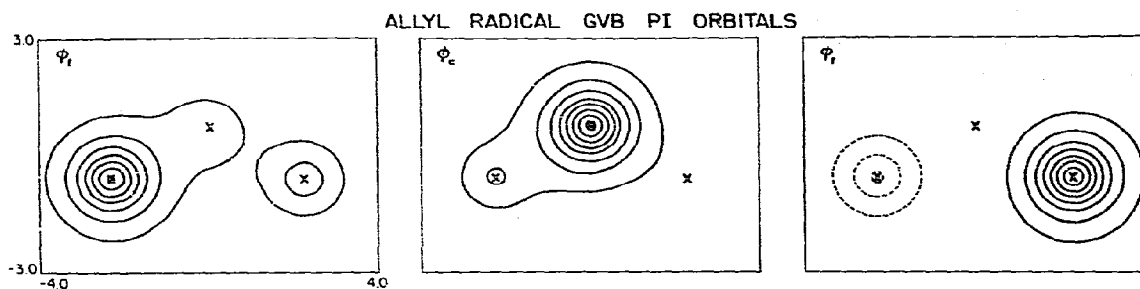


Fig. 1. GVB π orbitals for the localized wavefunction of allyl radical ψ_r (26). The overlap between the paired orbitals ϕ_1 and ϕ_2 is 0.719. The plotting plane is 0.5 bohr above the molecular plane with projected carbon atom positions indicated for clarity. The amplitude increment is 0.05 au.

short double bond to a symmetric geometry that can maximize electronic resonance. This acts to decrease the perceived resonance energy. Third, the ϵ_r we define compares the energy of the optimized GVB wavefunction ψ_r with the wavefunction Ψ_{res} in which the orbitals have not been reoptimized in the presence of the resonance. Including this reoptimization would increase ϵ_r . The close agreement between ϵ_r (9.8 kcal) and experiment (11 kcal) implies that these effects roughly balance. Work directed at quantifying these effects is currently in progress. Previous studies of the resonance in allyl using the full GVB method [3] (including optimization of spin coupling) yielded a resonance energy of

11.4 kcal. Use of a spatially projected GVB [4] wavefunction gave a value of 14.3 kcal. Each of those calculations used a frozen symmetric σ core taken from a Hartree-Fock (HF) calculation, as optimization of the σ orbitals was not feasible at that level of calculation.

The antiresonance energy ϵ_a is found to be 69.9 kcal, and decreases to 65.6 kcal if the GVB natural orbital coefficients are allowed to readjust in the presence of the resonance. This leads to a ${}^2A_2 \rightarrow {}^2B_1$ excitation energy of 75.6 kcal, which compares very well with the full π configuration interaction (CI) result of 75.4 kcal, indicating that the resonant-antiresonant description of these states is valid.

Table 1
Energies for allyl wavefunctions ^{a,b)}

Calculation	Single bonding structure ($H_{\epsilon\epsilon}$) (hartree)	Resonance state (2A_2) (hartree)	Resonance energy (ϵ_r) (kcal)	Antiresonance energy (ϵ_a) (kcal)	Excitation energy ${}^2B_1 \leftarrow {}^2A_2$ (kcal)
HF	-116.4130	-116.4129 ^{d)}	-	-	114.1
R-GVB ^{c)}	-116.4296	-116.4452	9.8	69.9	79.7
R-GVB(r) ^{d)}		-116.4454	10.0	65.6	75.6
full π CI ^{e)}		-116.4596	-	-	75.4

^{a)} All calculations use the symmetric geometry $R(CC) = 1.40 \text{ \AA}$, $R(C-H) = 1.08 \text{ \AA}$, all angles 120° .

^{b)} All calculations use the Dunning-Huzinaga valence double zeta basis (9s/5p) contracted to (3s/2p) for C and the scaled basis for H 4s to 2s (scaled by 1.2).

^{c)} One π bond was correlated, as indicated in (26).

^{d)} The CI coefficients for the natural orbital expression of the GVB wavefunction [see (21)] were allowed to reoptimize after including resonance. This is still rigorously a GVB wavefunction.

^{e)} The σ core was taken from the HF wavefunction of the 2A_2 state.

^{f)} Note that the symmetry-restricted HF solution has an energy 0.0001 hartree higher than the best HF wavefunction.

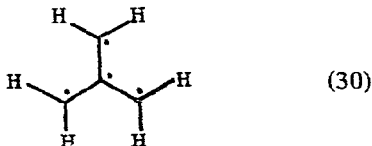
While a CI calculation can produce the most accurate results for a given basis set, it cannot yield conceptually important quantities like ϵ_a and ϵ_r .

4. Core ionization of N_2

Molecular orbitals of symmetric molecules are generally taken as symmetry functions for the symmetry group of the molecule. While this is appropriate for closed-shell molecules, some spectacular failures are known for open-shell molecules, where imposing symmetry upon the molecular orbitals leads to a much higher energy than if symmetry is relaxed. Well known examples include the lowest ionization of pyrazine [5],



and the singlet state of trimethylene methane [6],



A similar difficulty occurs upon ionizing electrons from core orbitals. Thus, for N_2 the ionization potential out of the $1s$ orbital is predicted to be almost 10 eV higher when symmetry orbitals are used to describe the ion state than when localized orbitals are used [7].

This indicates that the nature of the core ionized state is really that of a localized hole, which we can understand in the following way. The contribution each valence electron makes to the total energy goes roughly as the square of the effective nuclear charge (Z_{eff}) the electron "sees" (assuming hydrogenic behavior). For the case of the delocalized hole, each valence electron sees a new effective charge of $Z_{eff} + 0.5$, while for the localized case half the valence electrons see $Z_{eff} + 1.0$, while the other half see Z_{eff} . Since $(Z_{eff} + 1.0)^2 - Z_{eff}^2$ is always greater

than $2[(Z_{eff} + \frac{1}{2})^2 - Z_{eff}^2]$, more energy is gained by the localized hole. This is borne out by the fact that the relaxation energy for the localized ion is 16.5 eV (Koopmans' IP versus direct HF), which is very close to the 15.3 eV relaxation energy of the $1s$ ionized nitrogen atom, while the delocalized relaxation energy for N_2 is only 7.3 eV. While the core ion state has the nature of a localized hole, the total wavefunction should still retain the full molecular symmetry, and does if we take the linear combinations

$$\psi_g = \psi_\ell + \psi_r \quad (31a)$$

and

$$\psi_u = \psi_\ell - \psi_r \quad (31b)$$

where ψ_ℓ and ψ_r are the overlapping localized core hole wavefunctions.

The results of various calculations are shown in table 2. Calculations were carried out treating the neutral and ion states both at the HF level and with all valence electrons correlated, GVB(5/10). For the neutral the latter calculation leads to three bond pairs (σ , π_x , π_y) and two lone pairs ("2s") localized one on each N,



The delocalized HF calculations not only lead to an ionization potential 9.2 eV too large but they also lead to a g-u splitting energy 50% too large (0.126 versus 0.082 eV). Correlating the valence electrons leads to a slight decrease (0.32 eV) in the ionization potential and a slight increase in the splitting energy (0.082–0.093 eV). The final calculated ionization potential is 409.84 eV, in good agreement with the experimental value of 409.9 eV [8]. Such close agreement is fortuitous since correlation of the electron pair in the $1s$ orbital being ionized was not included (this would increase the ionization potential by ≈ 1 eV). Probably this error is balanced by some inadequacy in the basis set for describing the shape readjustment in the ion.

The very small resonant splittings are due to the very small overlap ($S_{\ell r} = 0.0023$) of the localized wavefunctions in (32).

Table 2
Ionization potentials for N_2^+

Level	Neutral ground state total energy (hartree)	Ionization potential (eV)			Splitting energy (eV)
		localized	${}^2\Sigma_u^-$	${}^2\Sigma_g^+$	
Basis I ^{b)}					
Koopmans' IP		427.59 ^{d)}	427.54	427.64	0.096
delocalized HF	-108.9059	-	420.28	420.41	0.124
localized HF		411.05	411.01 ^{e)}	411.09 ^{e)}	0.082
GVB 5/10	-109.9049	410.65	410.63 ^{e)}	410.72 ^{e)}	0.090
Basis II ^{c)}					
Koopmans' IP		426.81 ^{d)}	426.76	426.86	0.095
delocalized HF	-108.9808	-	419.41	419.53	0.126
localized HF		410.16	410.12 ^{e)}	410.20 ^{e)}	0.082
GVB 5/10	-109.0731	409.84	409.79 ^{e)}	409.88 ^{e)}	0.093
experiment ^{d)}			409.9		

^{a)} All calculations performed at experimental ground state geometry ($R_e = 1.09768 \text{ \AA}$) [12].

^{b)} Basis I is Huzinaga's (11s/7p) primitive gaussian basis contracted to (7s/4p), allowing four functions to describe the 1s orbital.

^{c)} Basis II is Huzinaga's (11s/7p) primitive gaussian basis contracted to (7s/5p) plus an optimized d exponent of 0.9 (further decontraction of the s and p was found unnecessary).

^{d)} Ref. [9]. ^{e)} These numbers result from the resonance of two overlapping wavefunctions.

^{f)} Localized Koopmans' IP values were obtained by forming a localized $\phi_{1s} = 2^{-1/2}(1\sigma_g + 1\sigma_u)$ and evaluating the ion energy with frozen orbitals.

Many previous calculations on core hole states of first-row diatomics have been performed [7-10] and the need for a localized description has been well established. The calculations presented here are the first to restore full symmetry to the ionic states while retaining a localized description.

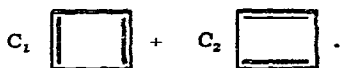
Müller et al. [7] have studied the effect of core hole localization on the predicted lineshape of the photoelectron peak. They found that while a delocalized hole predicts a linewidth too large by $\approx 80\%$, a localized hole description predicts a linewidth of 0.32 eV, in reasonable agreement with the experimental value of 0.42 eV. This agreement becomes even closer if one includes the peak broadening due to the 0.093 eV state splitting we calculate.

5. Discussion

One of the first studies of the importance of symmetry lowering in HF wavefunctions was the

work by Wadt and Goddard [5] on the n ion and $n\pi^*$ excitation states of pyrazine. They showed that the optimized wavefunction is localized but did not calculate the resonance energy by the R-GVB procedure. Instead, they converted the localized orbitals into a double set of symmetry orbitals and designed a CI calculation to mimic a resonating wavefunction. Recently Martin [11] tested these results for the positive ion by calculating the resonance energy of the localized HF wavefunction in the same fashion described in section 2. He found resonance energies essentially identical to those of Wadt and Goddard.

We have generalized this treatment to allow calculation of resonance interactions for correlated multiconfigurational wavefunctions. This is important since many electronic states are not adequately described at the HF level. This method is not limited to resonance of equivalent configurations, allowing treatment of resonance as a function of geometry, as in rectangular cyclobutadiene,



The remaining flaw in the resonating GVB approach is that the orbitals are calculated before resonating. As a result, the orbitals tend to delocalize in order to incorporate part of the resonance effect. We are currently developing an approach in which the orbitals are optimized in the presence of resonance, thus allowing each orbital to have the optimum shape for a particular localized form. This approach is more difficult than the usual self-consistent field methods because of the overlapping orbitals. It will be especially useful for cases where the delocalization tendency is so strong that the conventional wavefunction is totally delocalized.

We believe that the resonating GVB method will be useful both for quantitative and conceptual progress in analyzing wavefunctions: With this method, many complicated electronic states that previously required extensive CI calculations may be adequately described in terms of a small number of meaningful resonance contributors, a picture that is conceptually simple and chemically appealing.

Acknowledgement

The work was partially supported by a contract from the US Department of Energy (Contract No. DE-AC03-76SF00767, Project Agreement No. DE-AT03-80ER10608). The research reported in this paper made use of the

Dreyfus-NSF Theoretical Chemistry Computer which was funded through grants from the Camille and Henry Dreyfus Foundation, the National Science Foundation (Grant No. CHE78-20235), and the Sloan Fund of the California Institute of Technology.

References

- [1] W.A. Goddard III, *J. Chem. Phys.* 48 (1968) 450, and references therein.
- [2] S.W. Benson, *Thermochemical kinetics*, 2 Ed. (Wiley, New York, 1976) p. 309.
- [3] G. Levin and W.A. Goddard III, *J. Am. Chem. Soc.* 97 (1975) 1649.
- [4] G. Levin and W.A. Goddard III, *Theoret. Chim. Acta (Berl.)* 37 (1975) 253.
- [5] W.R. Wadt and W.A. Goddard III, *J. Am. Chem. Soc.* 97 (1975) 2034.
- [6] D.R. Yarkony and H.F. Schaefer III, *J. Am. Chem. Soc.* 96 (1974) 3754.
- [7] J. Müller, H. Agren and O. Goscinski, *Chem. Phys.* 38 (1979) 349.
- [8] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P.F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne and Y. Baer, eds., *ESCA applied to free molecules* (North-Holland, Amsterdam, 1969).
- [9] P.S. Bagus and H.F. Schaefer III, *J. Chem. Phys.* 56 (1972) 224.
- [10] H. Agren, L. Selander, J. Nordgren, C. Nordling, K. Siegbahn and J. Müller, *Chem. Phys.* 37 (1979) 161, and references therein.
- [11] R.L. Martin, W.R. Wadt and D.A. Kleier, Abstract of Talks Presented at the Second Annual West Coast Theoretical Chemistry Conference, California Institute of Technology, Pasadena, California, 9-11 April 1980.
- [12] K.P. Huber and G. Herzberg, *Molecular spectra and molecular structure: Constants of diatomic molecules* (Van Nostrand, Princeton, 1979).