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Reparametrizing MNDO for Excited-State Calculations by Using ab Initio Effective Hamiltonian Theory: Application to the 2,4-Pentadien-1-iminium Cation

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The ab initio effective valence shell Hamiltonian (H^v) theory is employed to reparametrize the standard MNDO Hamiltonian for MNDO-πCI (configuration interaction) excited-state calculations for the small, protonated Schiff base 2,4-pentadien-1-iminium. The revised parametrization, called H^{π}_{MNDO}, differs from the ground-state parametrization via adjustment of the basic p-orbital parameters: U_C, U_N, β_C, $G_{C,C}$, $G_{N,N}$. The β_C resonance integral is adjusted to remove all electron−electron correlation from the MNDO one-electron, two-center $H_{u,v}$ π-electron integrals. Likewise, a small correction of 0.25 eV is appended to both U_C and U_N. The MNDO ground-state $G_{C,C}$ and $G_{N,N}$ π-electron one-center, two-electron repulsion integrals are increased in value by about 1.5 and 2 eV, respectively, to reproduce the average of the ab initio H^v one-center, two-electron effective integrals. Subsequent H^{π}_{MNDO} calculations reproduce the lowest-lying *ab initio* H^v 20 vertical excitation energies to less than 0.2 eV on average (when full πCI is employed). We also estimate the size-consistency errors in previous ab initio MRSDCI calculations for the planar and twisted geometries to be as large as 0.2−0.3 eV. Thus, the MNDO-CI method has the potential of achieving excellent accuracy for similar molecules when properly parametrized.

I. Introduction

The electronically excited states of polyenes generate much theoretical interest because they play a key role in the function of many photoactive proteins such as the rhodopsin visual pigments, the pigment bacteriorhodopsin (BR), and other photoactive proteins (see refs 1−3). Historically, theoretical studies have utilized two seemingly diametrically opposed approaches: semiempirical methods and ab initio theory. The simple and efficient semiempirical methods permit detailed studies of the spectra and photodynamics of these chromophores in their natural environments. For example, the standard MNDO method has been reparametrized for excited-state configuration interaction (CI) calculations and used with reasonable success to examine the excited-state photodynamics of retinal,[4] to interpret the two-photon properties of bacteriorhodopsin,[5] and to suggest a model for the origins of photoreceptor noise in vertebrate rhodopsin.[6] Likewise, Warshel et al. employ the π-electron semiempirical theory QCFF-PI to study the photodynamics of the visual pigments.[2,7] Nevertheless, current semiempirical methods still lack the accuracy to fully resolve the issues surrounding the excited-state spectra and photodynamics of these systems. It is of interest to develop new and improved excited-state MNDO-CI methods[8,9] for treating biological chromophores such as protonated Schiff base polyenes.

In principle, ab initio techniques can provide the accuracy necessary to treat these large polyenes. However, the significantly increased memory and CPU requirements limit their application. Our goal is to exploit ab initio techniques to improve the accuracy and applicability of current semiempirical methods. Unfortunately, few studies attempt this approach because of the perceived incompatibilities between rigorous ab initio theories and phenomenological semiempirical methods. Indeed, some ab initio studies mistakenly criticize the basic foundations of semiempirical models.[10] The standard ab initio formulations mandate split-valence shell basis sets and different orbitals for each excited state, yet semiempirical methods utilize a minimal basis set of valence orbitals and the same core orbitals for all excited states. Further confusion arises because of limitations in the standard software packages. A recent theoretical study of the model Schiff base 2,4-pentadien-1-iminium (Figure 1) by Dobado and Nonella[11] shows that AM1-CI calculations, as implemented in MOPAC93, fail to reproduce ab initio MRSDCI calculations of the excited-state singlet potential energy surface. Implicit in their discussion of the AM1 method is the suggestion that such failure is inherent in the MNDO method. We demonstrate here, however, that given suitable parameterization, that MNDO-πCI calculations can yield accurate vertical excitation energies for all low-lying excited states.

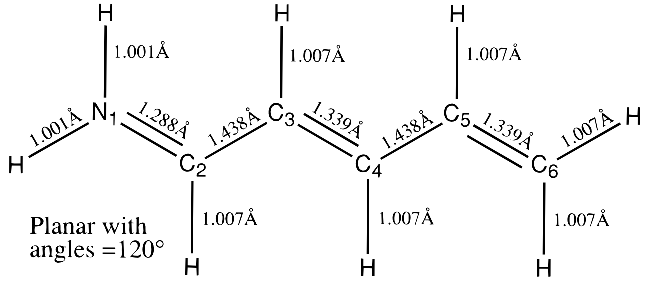

Figure 1. Geometry and atom numbering of the protonated Schiff base, 2,4-pentadien-1-iminium cation. This geometry was used in all calculations unless stated otherwise.

There does, in fact, exist a rigorous ab initio theory which not only produces highly accurate ab initio ground- and excited-state data but also provides an ab initio basis set for semiem-

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pirical theory. This method is called the effective valence shell Hamiltonian (H^v) theory.[9,12−16] Previous H^v calculations examined the excited states of 2,4-pentadien-1-iminium (see Figure 1)[12] and longer Schiff bases.[13] H^v vertical excitation energies for 2,4-pentadien-1-iminium compare to within 0.1−0.2 eV with other state-of-the-art ab initio calculations, such as MRSDCI calculations by Davidson[12] and others,[17] the CASSCF[17,18] and CASSCF+MP2 methods,[19,20] and the popular CASPT2 method.[21] The same calculations simultaneously provide π-electron effective integrals which are ab initio analogs of semiempirical parameters suitable for excited-state semiempirical calculations.

The ab initio effective integrals, being, in principle, exact, display a much richer structure than their semiempirical counterparts; they take on different numerical values, show a breakdown of transferability, and include three-electron integrals not present in semiempirical models. Here we explain how to use the H^v theory to reparametrize the readily available MOPAC93 semiempirical package for MNDO-πCI calculations on 2,4-pentadien-1-iminium. The first section clarifies the relationship between the ab initio H^v theory and the semiempirical MNDO-πCI calculations. The next section compares semiempirical MNDO-πCI Hamiltonian to ab initio H^v computed previously for a planar geometry of 2,4-pentadien-1-iminium.[12]

We explicitly explain how to compare the MNDO parameters to the H^v effective integrals and how to modify the MNDO p-orbital U_C, U_N, β_C, $G_{C,C}$, and $G_{N,N}$ to reproduce the lowest-lying ab initio H^v 20 vertical excitation energies to less than 0.2 eV on average. The third section considers why previous MNDO-PSDCI calculations yielded reliable results. Finally, the last section evaluates the accuracy of ab initio SDCI calculations on the excited-state potential energy surface for 2,4-pentadien-1-iminium. Approximate H^v calculations provide an estimate of the ab initio size-consistency errors associated with ab initio computations of the excited-state potential energy surface.[11] We also demonstrate that reparametrizing the MNDO-CI method for the ground-state spectra greatly improves the computation of the excited-state potential surface.

II. Theory: The Relationship between H^v and MNDO-πCI Calculations

The ab initio effective valence shell Hamiltonian (H^v) theory provides a route to developing new and improved semiempirical models and optimizing the parameters. Over the past few years research in H^v theory has pursued the following research goals:[12−16] (1) to provide an exact theory for semiempirical models, and, in particular, for π-electron theories;[22−25] (2) to implement the H^v method using standard ab initio electronic structure techniques on simple polyenes;[12,13,16,26−30] (3) to demonstrate that the H^v method provides state-of-the-art ab initio data which compares in accuracy with the best ab initio methods available such as MRSDCI[11,17] and CASSCF+MP2 and CASPT2 calculations;[19,21] (4) to test the basic assumptions of π-electron semiempirical methods on a number of model polyenes (these tests validate such approximations as the choice of the π-electron minimal basis set, a portion of the ZDO approximation, and the numerical values of many of the semiempirical parameters[29−32] and (5) to make the H^v theory more accessible to the general semiempirical community.

With items (1) through (4) now in place, it is appropriate to seek the goal of demonstrating how to apply the H^v approach to enhancing the reliability of current semiempirical methods.

First let us consider why we must reparametrize the ground-state MNDO Hamiltonian for excited states. A standard MNDO semiempirical calculation approximates the exact quantum mechanical ground-state electronic energy of a given molecule by using a phenomenological parameterization of the Hartree−Fock (HF) equations. Although the MNDO HF equations resemble the ab initio minimal basis set HF theory, a MNDO calculation *does not* approximate an ab initio minimal basis set HF calculation. Because the model has been parametrized against experimental data, it must approximate large basis set, fully correlated ab initio calculations. Therefore, the MNDO ground-state parameters must implicitly include the ab initio correlation contributions (including the corrections due to the larger basis set and correlation corrections to the Hartree−Fock wave function). A complete "ab initio" theory of semiempirical methods would specify explicitly how the ab initio correlation corrections enter into the ground-state semiempirical MNDO HF parameters.

Even without such a complete theory, it is intuitively obvious that the MNDO ground-state parameters cannot just be applied to excited-state CI calculations because the CI will then overcorrelate the ground state. Consider a MNDO-πCI calculation using the standard MNDO parameterization. The MNDO-πCI method first constructs the π-space CI matrix using the ground-state parameters as approximate valence electron interactions, but upon diagonalizing the πCI matrix, the ground state becomes correlated again. Because the HF MNDO parameterization already approximates the fully correlated ground state, the new CI ground state is overcorrelated. To avoid overcorrelation, MOPAC93 uses ground-state parameters in CI calculations of the excited states but provides both the HF and CI ground state as reference states. A more consistent approach would be to remove the empirical portion of the correlations from the ground-state HF parameters and just perform πCI calculations for both the ground and excited states. Such a procedure, however, will break down the MNDO assumptions of rotational invariance and parameter transferability and, consequently, require ad hoc procedures or significant modifications of the basic formalism.

The effective valence shell Hamiltonian (H^v) theory explains how to compute the effective valence electron interactions suitable for MNDO-πCI calculations for all states in a specific molecule. Consider performing MNDO-πCI calculations on the Schiff base polyene 2,4-pentadien-1-iminium. When the molecule is planar (see Figure 1), the six π-molecular orbitals (MOs) consist solely of linear combinations of the MNDO atomic p_π orbitals. Thus, a MNDO-πCI calculation resembles the semiempirical π-electron theory such as the familiar Pariser−Parr−Pople (PPP) method.[23−25] The effective valence shell Hamiltonian (H^v) theory provides ab initio effective integrals which directly correspond to the appropriate MNDO-πCI parameters.

How do these ab initio H^v π-electron effective integrals specifically relate to the standard MNDO parameters? The ab initio H^v takes the form

$$H^v = E_c + U_1^v + V_{1,2}^v + W_{1,2,3}^v + ... \qquad (1)$$

where E_c is the correlated core energy of the σ-framework, and U_1^v, $V_{1,2,}$ and $W_{1,2,3}^v$ are "effective" one-, two-, and three-electron valence shell operators, respectively. To a good approximation one may neglect the majority of the H^v integrals and simply relate traditional MNDO parameters to matrix elements of the corresponding H^v effective operators. Of course, the semiempirical parameters are expressed in a localized basis, so the H^v integrals must be transformed to a localized basis set, namely, to Löwdin orthogonalized atomic orbitals

(LO).[33,9] In the standard Dirac notation, the ab initio analogs of the MNDO-CI integrals take the form

$$U_u = \langle \mathrm{p}_u(1)|U_1^{\nu}|\mathrm{p}_u(1)\rangle \qquad (2)$$

$$H_{u,v} = \langle \mathrm{p}_u(1)|U_1^{\nu}|\mathrm{p}_v(1)\rangle \qquad (3)$$

$$G_{u,u} = \langle \mathrm{p}_u(1),\mathrm{p}_u(2)|V_{1,2}^{\nu}|\mathrm{p}_u(1),\mathrm{p}_u(2)\rangle \qquad (4)$$

$$\langle \mathrm{p}_u,\mathrm{p}_v|\mathrm{p}_w,\mathrm{p}_x\rangle = \langle \mathrm{p}_u(1),\mathrm{p}_v(2)|V_{1,2}^{\nu}|\mathrm{p}_w(1),\mathrm{p}_x(2)\rangle \qquad (5)$$

where U_u is the one-electron, one-center integral for LO p_u, $H_{u,v}$ is the two-center, one-electron integral between LOs p_u and p_v, and $G_{u,u}$ and $\langle \mathrm{p}_u,\mathrm{p}_v|\mathrm{p}_w,\mathrm{p}_x\rangle$ are the corresponding one-center and two-center two-electron integrals, respectively, in Dirac notation. Note that previous work on π-electron theory employs the Greek symbols $\beta_{u,v} = H_{u,v}$ and $\gamma_{u,u} = G_{u,u}$ for the π-electron effective integrals. Also, the MNDO matrix elements $H_{u,v}$ are parametrized by $H_{u,v} = S_{u,v}{}^1/_2(\beta_u + \beta_v)$, where $S_{u,v}$ is the atomic orbital overlap matrix and β_u and β_v are the optimized MNDO resonance parameters. The MNDO parameters U_u, β_u, and $G_{u,u}$ appear in MOPAC93 in the BLOCKDATA subroutine.

The comparison between the MNDO and H^{ν} integrals requires several modifications of the standard MOPAC93 program because the H^{ν} integrals are computed in a LO basis over the entire set of p_π atomic orbitals and because these integrals are appropriate for full πCI calculations. First, the MOPAC93 CI option automatically defines the six CI space molecular orbitals by selecting the three lowest energy HF occupied MOs and three highest orbital HF unoccupied MOs. But in 2,4-pentadien-1-iminium the lowest three MOs include a high-lying σ-orbital, so we have modified MOPAC93 to allow us to select the π-molecular orbitals. Second, MOPAC93 does not compute the two-center $H_{u,v}$ integrals directly. Therefore, we compute $H_{u,v}$ after performing the MNDO SCF calculation and then transform the MNDO one-electron $H_{u,u}$ and $H_{u,v}$ to the LO basis. Note that MOPAC already outputs the two-electron integrals in an orthogonalized basis. Third, the MOPAC93 multielectron configuration interaction (MECI) option is limited to a relatively small number of "microstates", or valence space slater determinants. Since the H^{ν} effective integrals are suited for full CI calculations, we interfaced MOPAC93 to the H^{ν} full CI program.

Finally, note that the MNDO assumptions of "rotational invariance" complicate the comparison between H^{ν} effective integrals and the MNDO parameters because the H^{ν} approach distinguishes between σ- and π-orbitals. To maintain rotational invariance, MNDO has the U_u, β_u, and $G_{u,u}$ parameters identical for all three p orbitals on atom u. This invariance must break down for MNDO-πCI calculations because the p_π and p_σ require different amounts of electron−electron correlation. The p_π orbitals lie in the valence space so correlation contributions must be removed from these interactions. The p_σ orbitals only contribute to the E_c correlated core energy (eq 1) and should remain unchanged. Because the MNDO rotational invariance is hard coded into the MOPAC93 program, removing correlation contributions from the MNDO p-orbital parameters actually corresponds to removing the correlation contributions from all p parameters. Nevertheless, E_c cancels when computing vertical excitation energies. Therefore it is not necessary to adjust the MNDO σ-orbital parameters. A complete MNDO-πCI reparametrization must also adjust the MNDO σ-orbital parameters (and possibly other terms) to reproduce the ab initio correlated energy of the σ-framework (E_c).

TABLE 1: Comparison of Selected H^{ν} Effective Integrals (eV) and Semiempirical MNDO p-Orbital[a] Parametrized Integrals (and MNDO One-Electron Parameters) for 2,4-Pentadien-1-iminium Cation at a Planar Geometry[b]

	bare	H^{ν}	MNDO	MNDO-B	H^{π}_{MNDO}
integral					
U_1	−50.4378	−47.1835	−45.2883	−45.3517	−46.2184
U_2	−46.6699	−44.8118	−44.5008	−44.5885	−45.0476
U_3	−47.1333	−44.2670	−44.5010	−44.5600	−45.0617
U_4	−44.7955	−42.6878	−42.8957	−42.9538	−43.4772
U_5	−41.7294	−39.7809	−39.6287	−39.6597	−40.1984
U_6	−34.9557	−34.8368	−34.0107	−34.0068	−34.5547
$H_{2,1}$	−3.7118	−3.6184	−3.0312	−3.6271	−3.6783
$\mathrm{H}_{3,2}$	−3.0273	−2.9126	−1.6345	−2.7245	−2.7355
$H_{4,3}$	−3.6317	−3.4648	−1.9819	−3.2953	−3.3201
$H_{5,4}$	−3.0904	−2.8604	−1.6346	−2.7205	−2.7342
$H_{6,5}$	−3.7094	−3.3768	−1.9839	−3.2948	−3.3165
$G_{1,1}$	19.8745	15.0405	12.98	12.98	15.04
$G_{2,2}$	16.7194	13.3508	11.08	11.08	12.80
$G_{3,3}$	16.8944	12.8183	11.08	11.08	12.80
$G_{4,4}$	16.8928	12.8049	11.08	11.08	12.80
$G_{5,5}$	16.8920	12.6269	11.08	11.08	12.80
$G_{6,6}$	16.3550	12.3566	11.08	11.08	12.80
parameter[c]					
U_C			−39.2056	−39.2056	−38.9556
U_N			−57.1723	−57.1723	−56.9223
β_C			−7.9341	−14.2800	−14.2800
β_N			−20.4958	−20.4958	−20.4958
$G_{\mathrm{C,C}}$			11.08	11.08	12.80
$G_{\mathrm{N,N}}$			12.98	12.98	15.04

[a] No s-orbital integrals or parameters shown. [b] Calculations described in text. [c] MNDO p-orbital one-electron parameters.

III. Results and Discussion

A. Comparison between H^{ν} and MNDO-πCI Integrals for 2,4-Pentadien-1-iminium. The ab initio H^{ν} being, in principle, exact, has many more effective integrals than the semiempirical counterparts. The H^{ν} contains not only all one- and two-electron effective integrals, including those neglected in the NDO approximations, but also three- and four-electron effective integrals. Nevertheless, previous protonated Schiff base calculations demonstrate that these integrals contribute only a few tenths of 1 eV to the vertical excitation energies.[12,33] The remaining small set of ab initio integrals display unique geometry dependencies which cannot be accounted for easily within the MNDO framework. Therefore, we wish to determine the minimal number of corrections necessary to modify the currently available MOPAC93 program to adjust the MNDO ground-state parametrization to reproduce the ab initio excited-state spectra with ab initio accuracy (at least 0.3 eV[21]).

A recent H^{ν} study computes the compete set of π-electron effective integrals for the 2,4-pentadien-1-iminium cation at a particular, planar geometry[12] (see Figure 1). Because the H^{ν} effective integrals depend on the molecular geometry, we compare the H^{ν} integrals to the MNDO π-electron parameters for 2,4-pentadien-1-iminium, employing the same geometry as the ab initio calculations. Table 1 summarizes selected H^{ν} effective integrals and the standard MNDO integrals, in the localized, Löwdin orthogonalized basis of p_π orbitals. Table 1 only lists the bare valence shell interactions for comparison. (We only consider the semiempirical MNDO parametrization because compared to the differences between the H^{ν} and MNDO integrals, the deviations between the MNDO, AM1, and PM3 parametrizations are insignificant.) Table 1 also presents two other parametrizations, denoted MNDO-B and $\mathrm{H}^{\pi}_{\mathrm{MNDO}}$, explained below.

The most obvious differences between the MNDO and H^{ν} Hamiltonians arises in the ground-state MNDO π-electron two-center $H_{u,v}$ integrals. The MNDO $H_{u,v}$ values differ by 1 eV or more from their ab initio πCI value, as computed in the Löwdin orthogonalized basis, and by about a factor of 2 when in the nonorthogonal atomic orbital basis (not shown). In fact, the third-order H^v $H_{u,v}$ values only differ from the bare 1-electron, 2-center integral by at most 0.1−0.2 eV, indicating that the higher order perturbation corrections to the $H_{u,v} = \langle p_u(1)|U_1^v|p_v(1)\rangle$ effective integrals mostly cancel. Thus, the ground-state MNDO $H_{u,v}$ parameter requires empirical corrections to mostly account for the "nondynamical" correlations among the π-electrons which appear in the ground-state wave function after diagonalizing the πCI matrix—at least for protonated Schiff base polyenes.

The one-center $U_u = H_{u,u}$ parameters require only small amounts of correlation, and the current model for U_u reproduces U_N and the geometry-dependent U_C quite well. First, note that the correlations contribute most strongly near the NH_2^+ moiety. The bare U_N value is about 50.4 eV while the third-order U_N contains 3.2 eV of correlation, whereas the bare and effective U_{C6} differ by only 0.1 eV. Second, despite the wide variation in correlation contributions to U_u matrix elements, the MNDO model recovers over 98% of these effective integrals. The H^{π}_{MNDO}, U_N and U_{C6} parameters are −46.4 and −35.4 eV, which only differ from the H^v values by 0.8 and 0.6 eV, respectively.

The largest correlation contributions enter the two-electron $G_{C,C}$ and $G_{N,N}$ effective Coulomb interaction, thus H^v effective integrals display the strongest deviations from the MNDO one-center, two-electron parameters. The ab initio effective π-electron $G_{C,C}$ vary by 0.5 eV or more between different carbon centers. The variation in $G_{C6,C6}$ arises from atomic orbital overlap, and more sophisticated MNDO methods, such as MNDOC, may account for such effects.[9] But the variation in $G_{C2,C2}$ results purely from electron−electron correlation effects due to the nearby NH_2^+ group, and no current semiempirical methods model such variations. Generally the H^v $G_{C,C}$ and $G_{N,N}$ are 1.5−2 eV larger than the standard MNDO values, and can vary by up to 1 eV depending on the molecular environment. The MNDO $G_{N,N} = 12.98$ eV whereas the ab initio $G_{N,N} = 15.04$ eV for 2,4-pentadien-1-iminium. H^v calculations on larger Schiff bases indicated that the ab initio $G_{N,N}$ and other $G_{C,C}$ values do not stabilize until the Schiff base has at least four double bonds.[13] For instance, $G_{N,N} = 15.25$ eV for propeminium ($C_3H_4NH_2^+$) and 13.67 for the longer $C_7H_8NH_2^+$ Schiff base (as computed using the third-order H^v).

The remaining MNDO π-electron integrals do differ from the ab initio H^v effective interactions, but not so significantly to warrant further investigation here. In particular, the other two-electron Coulomb MNDO integrals ($\langle p_u,p_v|p_u,p_v\rangle$) differ by 0.1−0.65 eV from the H^v $\langle p_u(1),p_v(2)|V^v_{1,2}|p_u(1)p_v(2)\rangle$ effective integrals, with the largest deviations at short range. And, as discussed above, the MNDO U_u parameters recover 98% of the ab initio values. Thus, to correct the ground-state MNDO parametrization for MNDO-πCI calculations, the π-electron CI correlations must be removed from the ground-state MNDO two-center $H_{u,v}$ and one-center $G_{C,C}$ and $G_{N,N}$ π-electron effective integrals, whereas the remaining MNDO-CI π-electron integrals can then be computed using the standard MNDO functional forms.

We can understand why the ab initio H^v $G_{C,C}$ depends on its molecular environment by contrasting the development of semiempirical π-electron and all-valence-electron methods.[9,22,24,25,34−37] Historically $G_{C,C}$ has been taken as it was in the original π-electron (i.e. Pariser−Parr−Pople) theories, namely, the experimental carbon atom ionization potential (IP) minus the electron affinity (EA):

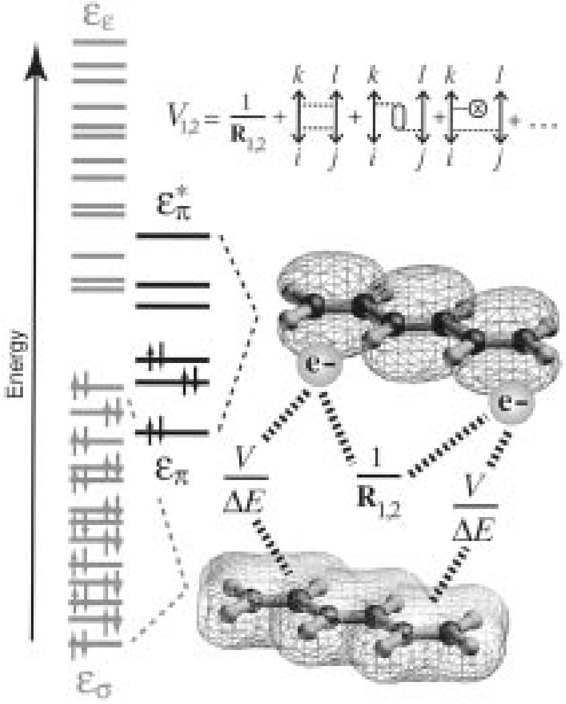

Figure 2. Schematic representation of the first two contributions to the effective Coulomb interaction, the bare space (R_{12}^{-1}) interactions, and the second-order (folded) ladder diagram. The bare space interaction, R_{12}^{-1}, couples the π-electrons, e^-, directly through space, while the perturbative corrections, such as the ladder diagram, couples the π-electrons via scattering into the σ-framework. The equation at top provides a diagrammatic expression for the dominant, second-order contributions to the effective Coulomb interaction, V_{12}, which includes R_{12}^{-1}, three dominant second-order contributions (ladder, RPA, and single-particle interaction Brandow diagrams), and additionally, numerous third-order contributions (indicated with the ellipses).

$$G_{C,C} = IP(C) - EA(C) \tag{6}$$

Modern π-electron theory recognizes that $G_{C,C}$ should depend on the molecular environment; however, in the all-valence-electron semiempirical theories $G_{C,C}$ is a fixed value.[25] Again, the breakdown of the MNDO rotational invariance implies that the exact MNDO-πCI parameters should resemble more modern π-electron theories.

Further insight into the geometry dependence of $G_{C,C}$ comes from examining the ab initio equations for the matrix elements of the $V^v_{1,2}$ effective operator (the effective integrals). For example, consider the second-order ladder-type diagrams presented below (and schematically in Figure 2)[15]

$$\langle p_i(1),p_j(2)|V^v_{1,2}|p_l(1),p_k(2)\rangle = \left\langle p_i(1),p_j(2)\left|\frac{1}{R_{1,2}}\right|p_l(1),p_k(2)\right\rangle + {}^1/_4 \sum_{\alpha,\alpha'} \frac{\tilde{v}_{ij,\alpha,\alpha',kl}}{\epsilon_k + \epsilon_l - \epsilon_\alpha + \epsilon_{\alpha'}} + {}^1/_4 \sum_{c,c'} \frac{\tilde{v}_{ij,c,c'}\tilde{v}_{c,c',kl}}{\epsilon_k + \epsilon_l - \epsilon_c + \epsilon_{c'}} + \ldots \tag{7}$$

where ϵ_i denotes the energy of the π-molecular orbital p_i and the valence orbital indices i, k, and l refer to the valence spin orbitals, the sum over α and α′ ranges over all valence and excited spin orbitals, except that α and α′ cannot both simultaneously be valence spin orbitals, and

$$\tilde{v}_{ij,kl} = \left\langle \mathrm{p}_i(1),\mathrm{p}_j(2)\left|\frac{1}{R_{1,2}}\right|\mathrm{p}_k(1),\mathrm{p}_l(2)\right\rangle - \left\langle \mathrm{p}_i(1),\mathrm{p}_j(2)\left|\frac{1}{R_{1,2}}\right|\mathrm{p}_l(1),\mathrm{p}_k(2)\right\rangle \quad (8)$$

As seen in Figure 2, the effective Coulomb interactions consist of a direct, through-space (or bare) interaction ($1/R_{1,2}$) and indirect, virtual (or effective) interactions ($V/\Delta E$). The effective interactions couple the two valence electrons indirectly through the σ-framework (c,c') and the other valence and excited (α,α') orbitals. The exact ab initio expressions for $G_{\mathrm{C,C}}$ and $G_{\mathrm{N,N}}$ must then clearly depend on their molecular environment to some extent, but only ab initio calculations can elucidate these variations.

The valence shell effective interactions also display spatial locality in that the electrons closest in space interact the most strongly. The largest correlations appear in effective Coulomb integrals $G_{\mathrm{C,C}}$ and $G_{\mathrm{N,N}}$ and $G_{\mathrm{N,N}}$ because the valence electrons reside in the same atomic orbital. Likewise, the $H_{u,v}$ integrals require far less correlation because the effective U_1^{ν} operator only renormalizes the interactions for one valence electron.

B. Constructing the MNDO-πCI Parametrization for 2,4-Pentadien-1-iminium. The H^{ν} Schiff base calculations demonstrate that the bulk of the πCI parametrization enters the ground-state MNDO $H_{u,v}$, $G_{\mathrm{C,C}}$, and $G_{\mathrm{N,N}}$ parameters, so by adjusting these parameters MNDO-πCI calculations should reproduce ab initio H^{ν} vertical energy differences for this small polyene.

Because our ab initio calculations serve as the reference for evaluating the new MNDO-πCI parametrization, let us first qualify the accuracy of the ab initio H^{ν} excited-state calculations. The H^{ν} spectrum reported here arises from the third-order H^{ν}_{3rd} computations which employ “constrained” molecular orbitals and which retain all effective integrals.[12] In neutral polyenes, constrained calculations misrepresent electronic states which require large polarization and Rydberg contributions.[33] The most accurate H^{ν} calculations generally employ unconstrained, or “full” valence spaces, which include more of the orbital polarization corrections and additional Rydberg orbitals. Protonated Schiff bases do not require the additional Rydberg orbitals, and the lowest singlet states require less polarization contributions.[12] Therefore, the constrained orbitals perform well for describing the low-lying states. This observation also explains why the Schiff base model Hamiltonians perform well even though they lack three-electron interactions; the H^{ν} three-electron operators describe, at lowest order, ab initio orbital polarization corrections.[12,33] Polarization corrections will become more important for the higher-lying excited states and for the low-lying singlet states at twisted geometries.[11]

We present a much larger portion of the low-lying spectrum of valence-like states than previously reported in order to demonstrate how well the new MNDO-πCI parametrization performs. Because the H^{ν} approach calculates the effective operator itself, a single ab initio calculation yields all π-electron valence states. In contrast, the MRSDCI and CASSCF+MP2 methods require seperate calculations for every excited state. Although the H^{ν} constrained calculations may err for the higher-lying states, since no other ab initio data is available for comparison we have arbitrarily chosen to evaluate the lowest 20 excited states for our reference spectrum. In practice one should not expect MNDO-πCI calculations to reproduce all electronically excited π-state excitation energies because the MNDO Hamiltonian lacks explicit three-electron operators.

Table 1 lists parameters for three different MNDO-CI parametrizations, denoted as MNDO, MNDO-B, and H^{π}_{MNDO}. The MNDO-B parametrization only modifies the MNDO β_{C}, rescaling it by a factor of 1.8 (shown in Table 1). This effectively removes the correlation contributions from the $H_{u,v}$ matrix elements since the MNDO model has $H_{u,v} = S_{u,v}{}^{1}/_{2}(\beta_u + \beta\nu)$, where $S_{u,v}$ is an atomic orbital overlap matrix. Note that reseting β_{C} also modifies the values of U_{C} and U_{N} listed because Table 1 presents these integrals in a Löwdin orthogonalized basis. (It is also possible to further adjust the MOPAC $H_{u,v}$ integrals by scaling the $S_{u,v}$ p-orbital overlap matrix. This is sometimes refered to as adjusting the π-orbital mobility.[5] (See subsection III.C below.)

TABLE 2: Comparison of Computed Low-Lying Excitation Energies (eV) for the 2,4-Pentadien-1-iminium Cation[a]

state	H^{ν}	MNDO	MNDO-B	H^{π}_{MNDO}	H^{ν}-SDCI
singlets					
2^1A′	4.50	2.91	4.60	4.67	4.72
3^1A′	5.80	3.14	6.25	6.06	6.00
4^1A′	7.13	4.89	6.80	6.90	7.47
5^1A′	8.01	5.33	7.09	8.11	8.38
6^1A′	8.26	5.90	8.00	8.61	8.61
7^1A′	9.42	6.31	8.88	9.40	9.80
8^1A′	9.64	6.50	9.28	9.70	9.97
9^1A′	10.14	6.97	9.70	10.20	10.64
10^1A′	10.89	7.27	10.37	11.02	11.36
triplets					
1^3A′	2.76	1.86	3.09	2.84	3.09
2^3A′	4.68	2.90	5.04	4.57	5.07
3^3A′	6.02	3.67	6.25	5.67	6.42
4^3A′	6.47	4.47	6.80	6.43	6.97
5^3A′	7.33	5.00	8.14	7.53	7.69
6^3A′	7.66	5.64	8.29	7.97	7.95
7^3A′	9.00	5.77	9.43	8.65	9.14
8^3A′	9.46	6.51	9.96	9.72	9.86
9^3A′	9.86	6.76	10.12	10.10	10.32
10^3A′	10.78	7.21	10.37	10.50	11.17
quintets					
1^5A′	9.01	5.64	9.95	8.85	9.14
⟨Error⟩[b]		−2.66	0.08	0.01	0.35
⟨|Error|⟩[c]		2.67	0.46	0.19	0.35

[a] Calculations described in text. [b] Average error. [c] Average absolute error.

The $\mathrm{H}^{\pi}_{\mathrm{MNDO}}$ additionally adds 0.25 eV to U_{C} and U_{N}, plus it resets the $G_{\mathrm{N,N}}$ and $G_{\mathrm{C,C}}$ parameters to 15.04 and 12.8 eV, respectively. The adjustment of the U_{C} and U_{N} brings these semiempirical parameters in closer agreement with the ab initio values, although it modifies $H_{u,v}$ values as well. The new $G_{\mathrm{N,N}}$ one-center, two-electron parameters now equal the ab initio $G_{\mathrm{N,N}}$ value. Whereas the new $G_{\mathrm{C,C}}$ parameter is taken as the average ab initio $G_{\mathrm{C,C}}$ value, the MOPAC program expects all $G_{\mathrm{C,C}}$ parameters to have the same value. After reseting β_{C}, $G_{\mathrm{N,N}}$, and $G_{\mathrm{N,N}}$, and $G_{\mathrm{C,C}}$ in the MOPAC93 program (in the BLOCKDATA subroutine), the remaining MNDO integrals (U_{C}, U_{N}, and all remaining two-electron integrals $\langle \mathrm{p}_u,\mathrm{p}_v|\mathrm{p}_w,\mathrm{p}_x\rangle$) arise from the standard MNDO formulas.

Table 2 tabulates spectra from the ab initio H^{ν} and three seperate MNDO-πCI (MNDO, MNDO-B, and H^{π}_{MNDO}) calculations. (It also includes a calculations denoted as H^{ν}-SDCI, which is used to estimate the magnitude of ab initio size consistency corrections.) All of the calculations have six π-molecular orbitals in the valence space and diagonalize the full πCI matrix. The ground-state MNDO parametrization performs extremely poorly for excited-state MNDO-πCI calculations, as noted previously. With the simple correction of the inaccurate β_{C} MNDO parameter, however, the MNDO-B πCI calculations reproduces the 9 lowest-lying ab initio H^{ν} singlet excited states quite well. The average error (⟨Error⟩) from the H^{ν} data is a mere −0.08 eV. The average absolute error (⟨|Error|⟩), however, is a much larger 0.46, indicating large fluctuations. Nevertheless, the MNDO-B model provides a far superior description compared to the severely defficient standard MNDO-CI calculations.

The H^{π}_{MNDO} model describes the entire spectrum of the excited states much better over all, with similar errors but smaller fluctuations. The average error from the ab initio H^{v} calculations is a miniscule 0.01 eV, and the average absolute error is now only 0.18 eV! Note, however, that adjusting the $\gamma_{\mathrm{C,C}}$ and $\gamma_{\mathrm{N,N}}$ integrals raises the lowest singlet state and lowers the first triplet. Additionally, both of the two lowest excited singlets remain 0.1−0.2 eV too high in both the MNDO-B and H^{π}_{MNDO} models. A more optimal H^{π}_{MNDO} model must further optimize the MNDO one-electron parameters in order to reproduce the ab initio U^{v}_{1} operator more accurately. Corrections include both employing a better parameter optimization method (such as a genetic algorithms approach) and improving the MNDO functional form for the one-electron operator. Further corrections might then model the environmental dependence of the $\gamma_{\mathrm{C,C}}$ effective integrals.

C. Analysis of Other MNDO-CI Parametrizations. A number of semiempirical methods treat excited states of protonated Schiff bases, including PPP, ZINDO, and MNDO-CI methods.[2,5,7,9,22,34] In particular, MNDO-PSDCI calculations have been used to interpret the spectroscopy and photodynamics of retinal and its analogs.[1,4−6] It is of interest to compare the MNDO-PSDCI semiempirical excited-state method to the ab initio theory in order to understand why MNDO-PSDCI performs so well.

The MNDO-PSDCI parametrization corrects the MNDO one-electron one-center $H_{u,v}$ integrals by rescaling the MNDO β_{C} parameter by 2.48 and then reducing the π-mobility by the factor 0.75.[5] Thus the MNDO-PSDCI calculations resemble the MNDO-B calculations described above, and it is expected that this MNDO-PSDCI parametrization should describe low-lying excited singlet states of Schiff bases quite well—at least for planar geometries. Figure 3 compares MNDO-PSDCI calculations of the low-lying excited states of the 2,4-pentadien-1-iminium cation with the other theoretical treatments examined here. As seen, the MNDO-PSDCI method does indeed perform quite well for the low-lying excited singlet states, even though it employs both SDCI approximations and an empirically derived parametrization. The MNDO-PSDCI excited singlet states only differ from the ab initio H^{v} energies by 0.22−0.23 eV on average, with all transitions lower in energy than those calculated via the ab initio procedures. The semiempirical treatment actually outperforms the only slightly approximate H^{v}-SDCI calculation, which is systematically too low by 0.35 eV on average. In general, the MNDO-PSDCI errors lie within the standard accepted values for state-of-the-art ab initio calculations for the excited states of polyenes[21] and at a fraction of the cost of the ab initio calculations.

D. Evaluation of ab Initio SDCI Calculations on 2,4-Pentadien-1-iminium. Finally, we wish to evaluate the accuracy of previous ab initio MRSDCI calculations on both the spectra and the excited-state potential energy surface. The ab initio H^{v} method is fully size-extensive and size-consistent, the perturbative equivalent of the more familiar MRSDCI method. As such, one expects both methods to yield similar results when employing roughly the same active spaces and ab initio primitive basis sets. Furthermore, we can estimate the size-consistency errors associated with such CI calculations by diagonalizing an approximate H^{v}-πCI matrix which includes only singles and doubles excitations out of a HF-like reference state rather than the full πCI matrix. We denote such calculations as the H^{v}-SDCI approximation. This approximation does not fully reproduce the size-consistency errors in MRSDCI calculations; however, it does provide a crude estimate, plus it mimics the MNDO-SDCI approximations commonly employed in semiempirical excited-state calculations.

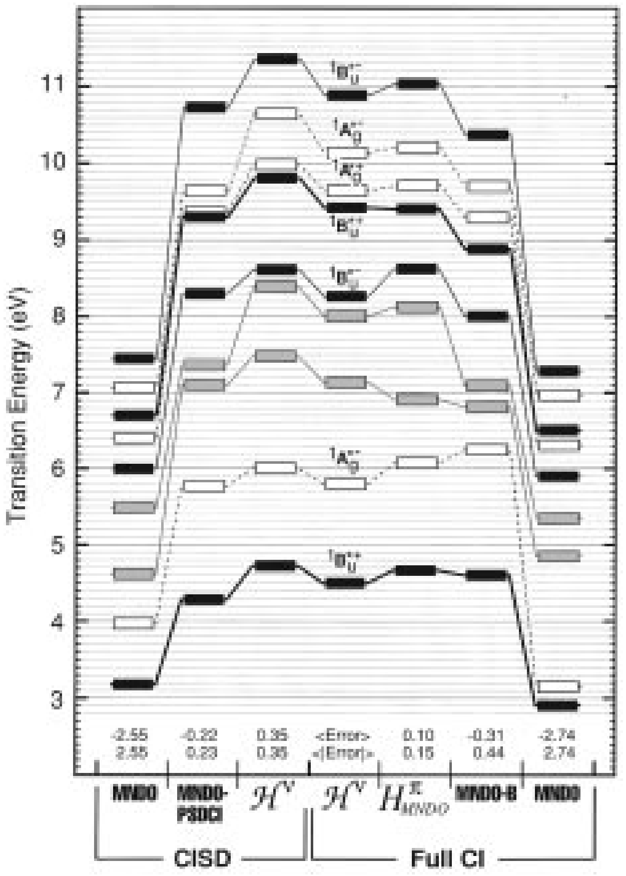

Figure 3. Schematic comparison of selected ab initio and semiempirical excited singlet state calculations for the 2,4-pentadien-1-iminium cations. Symmetry labels are very approximate and are based on a correlation analysis with respect to the excited singlet state manifold of *all-trans*-hexatriene. The MNDO-PSDCI calculations used the standard MNDO parameters with the following exceptions: U_{ss}(carbon) = −54.37093 eV, U_{ss}(oxygen) = −102.63364 eV, U_{pp}(oxygen) = −80.13140 eV, β_{p}(carbon) = −19.67662 eV, β_{p}(oxygen) = −42.49451 eV, σ-mobility constant = 1.25, π-mobility constant = 0.75, R_{ij} (repulsion correlation length) = 1.33 Å. All (9) singles and (45) doubles from the π and π^* orbitals were included, and transition energies are relative to the correlated [$E(\mathrm{S}_0) = -0.8066$ eV] ground state.

Table 2 lists the results of H^{v}-SDCI calculations on the spectra of 2,4-pentadien-1-iminium. Both the average error and the average absolute error are 0.35 eV, which are, in fact, greater than the errors associated with the simple semiempirical H^{π}_{MNDO} calculations. The so-called "semiempirical" approximation to the H^{v} operator actually yields errors of the same magnitude as the "ab initio" errors involved with SDCI calculations.

Table 3 presents calculations of the vertical excitation energies (in eV) for 2,4-pentadien-1-iminium with a 6-31G* basis set and the middle double bond rotated to 90°. (The exact geometry is the (90, 180) geometry presented in ref 11.) The H^{v} and MRSDCI calculations therefore utilize the exact same geometry and basis set and should yield similar results. Additionally, the H^{v} calculations employ optimized "full" orbitals rather than semiempirical-like "constrained" orbitals.[12,33] The MRSDCI excitation energy is 0.82 eV (18.9 kcal/mol)[11] whereas the H^{v} energy is much smaller 0.53 eV (12.2 kcal/mol). The H^{v}-SDCI

TABLE 3: Comparison of Computed Low-Lying Excitation Energies (eV) for the 2,4-Pentadien-1-iminium Cation at a Twisted Geometry[a]

state	H^{v} [b]	H^{v}-SDCI	H^{π}_{MNDO} [c]	MRSDCI[d]
singlets				
2S	0.53	0.74	0.25	0.82
3S	4.48	4.70	3.78	
4S	5.00	4.79	5.60	
triplets				
1T	0.50	0.71	0.22	
2T	2.95	3.32	2.94	
3T	3.68	3.98	3.72	

[a] Geometry (90, 180) taken from ref 12, in which the polyene middle double bond is twisted to 90°. [b] H^{v} calculations employ the 6-31G* basis set and six "full" valence orbitals. [c] MNDO-CI calculations utilize the six valence orbitals with minimal s-orbital occupation. [d] Reference 11.

excitation energy, which lacks some size-consistency corrections, is a larger 0.74 eV (17.1 kcal/mol). Hence, we can crudely estimate the size-consistency errors in the MRSDCI calculations to be 0.2−0.3 eV (4−7 kcal/mol).

In light of the size-consistency errors associated with the ab initio calculations, consider now how well H^{π}_{MNDO} calculations reproduce the vertical excitation energies of the twisted polyene. The lowest singlet state lies at 0.25 eV, 0.2−0.3 eV lower than the ab initio H^{v} calculations. The second excited singlet fares much worse, being 0.6 eV too low in energy. The low-lying triplets all appear very accurate. Nevertheless, the general result holds that the semiempirical H^{π}_{MNDO} calculations perform as well as the ab initio MRSDCI calculations for the first singlet state when considering that the MRSDCI calculations include large (4−7 kcal/mol) size-consistency errors.

E. Comments and Conclusions. The effective valence shell Hamiltonian (H^{v}) theory provides a rigorous means to reparametrize semiempirical methods using state-of-the-art ab initio data. While some ab initio studies disavow semiempirical methods,[10,11] none offer any practical solutions to correcting the basic models. A recent ab initio study demonstrates that the standard AM1-CI calculations, as implemented in MOPAC93, cannot produce reasonbly accurate excited states or potential energy surfaces for the small, protonated Schiff base 2,4-pentadien-1-iminium.[11] Here we show how to use ab initio H^{v} calculations to reparametrize the ground-state MNDO method to treat excited-state spectra with ab initio accuracy (less than 0.3 eV[21])—at least at planar geometries. The new parametrization requires only trivial modifications to the standard MOPAC93 computer program. We then explain why previous MNDO-PSDCI calculations have worked so well.

Earlier H^{v} calculations already consider 2,4-pentadien-1-iminium, providing a reference spectrum of all low-lying π-electron excitation energies. The same calculations also yield detailed insight into how to adjust the standard MNDO ground-state parameters for excited-state πCI calculations. We construct a new H^{π}_{MNDO} parametrization that only requires reseting the numerical values of the MNDO ground-state p-orbital parameters U_{C}, U_{N}, β_{C}, $G_{\mathrm{C,C}}$, and $G_{\mathrm{N,N}}$ to more closely reproduce the ab initio values of the corresponding H^{v} effective integrals. The MNDO β_{C} should be adjusted as to remove all electron−electron correlation from the MNDO one-electron, two-center $H_{u,v}$ π-electron integrals. The MNDO ground-state $G_{\mathrm{C,C}}$ and $G_{\mathrm{N,N}}$ π-electron parameters should be increased in value by about 1.5 and 2 eV, respectively, to reproduce the average of the H^{v} $\langle \mathrm{p}_u(1),\mathrm{p}_v(2)|V^{v}_{1,2}|\mathrm{p}_w(1),\mathrm{p}_x(2)\rangle$ effective integrals. Even though this new H^{π}_{MNDO} parametrization does not incorporate the full complexity of the ab initio effective integrals, which includes environmentally dependent $G_{\mathrm{C,C}}$ integrals, three-electron effective integrals ($\langle \mathrm{p}_u(1),\mathrm{p}_v(2),\mathrm{p}_w(3)|W^{v}_{1,2,3}|p_x(1),\mathrm{p}_y(2),\mathrm{p}_z(3)\rangle$), etc., the H^{π}_{MNDO} calculations reproduce the lowest-lying, constrained ab initio H^{v} 20 vertical excitation energies to within 0.2 eV on average.

Modern semiempirical theories actually retain the original $G_{u,u} = \gamma_{u,u}$ Coloumb integrals and adjust the $H_{u,v} = \beta_{u,v}$ integrals (MNDO adjusts β_u and β_v) to fit experiment. But it is now evident that the ab initio $H_{u,v}$ π-electron effective integrals contain only 0.1−0.2 eV of electron correlation—at least in protonated Schiff base polyenes—and therefore the MNDOπ-CI parametrization need only adjust β_u and β_v to reproduce the bare $H_{u,v}$ integrals. The standard PPP $\beta_{u,v}$ contains far too much correlation for πCI calculations, and is about 1 eV too small for protonated Schiff bases.[38] This is because the $\beta_{u,v}$ were transfered from neutral polyenes, but the $\beta_{u,v}$ in neutral polyenes also includes averages of additional two- and three-electron effective integrals ($\langle \mathrm{p}_u(1),\mathrm{p}_v(2),\mathrm{p}_w(3)|W^{v}_{1,2,3}|\mathrm{p}_x(1),\mathrm{p}_y(2),\mathrm{p}_z(3)\rangle$) in order to account for polarization and Rydberg contributions absent from the constrained PPP valence space.[30,9] The protonated Schiff bases do not require these contributions in their low-lying electronic states, and so the $H_{u,v} = \beta_{u,v}$ parameters require virtually zero correlation.

The ab initio H^{v} calculations also provide an estimate of the size-consistency errors associated with previous ab initio MRSDCI calculations of the excited state of this small, protonated Schiff base polyene. We estimate these errors to be 0.2−0.3 eV (4−7 kcal/mol). Additionally, we show that semiempirical H^{π}_{MNDO} calculations perform reasonably well for the twisted polyene given the accuracy of state-of-the-art ab initio theory. In particular, the H^{π}_{MNDO} calculations reproduce the energy gap between the ground- and excited-state potential energy surfaces to within the 0.2−0.3 eV error range expected from current excited-state theory. One should also bear in mind that even MRSDCI excited-state potential energy surfaces may not properly describe the excited-state photodynamics of this small polyene and that further theoretical work is certainly in order.[39,40]

The calculations presented here elucidate how to immediately apply H^{v} calculations to improve traditional semiempirical models without having to construct a completely new semiempirical method from scratch. It is hoped that this study will serve to motivate further basic and applied research on the H^{v} approach. Future applied studies could focus on extending the H^{π}_{MNDO} method for more accurately treating excited-state potential energy surfaces of the protonated Schiff bases, examining other photoactive proteins, and incorporating transition dipole moments and transition metals into the H^{π}_{MNDO} method. In particular, an improved H^{π}_{MNDO} theory for twisting of polyenes should, however, break the MNDO assumption of rotational invariance and utilize different parameters for those orbitals lying inside and outside the CI active space. Likewise, semiempirical MCSCF calculations in general should employ two different parametrizations: one suitable for core orbitals and one suitable for active space orbitals.

Future research will focus on two outstanding problems in H^{v} theory which will reduce the computational and mathematical complexity of the theory by several orders of magnitude. First, to obtain just a few parameters, such as $G_{\mathrm{P,P}}$, one must presently compute all possible two-electron integrals. New studies will attempt to obtain the H^{v} effective integrals directly in a localized basis of valence orbitals, thus reducing the computation time by several orders of magnitude. Second, the current second-order theory does not provide optimal $G_{P,P}$ effective integrals, at least for small systems, and generally third-order calculations are necessary. Consequently, future work will also consider techniques for utilizing the second-order theory to provide useful ab initio analogs of semiempirical parameters.

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IV. Appendix

The ab initio H^v calculations discussed here have been described in more detail first in the original work by Freed on the third-order H^v theory[15] and its application to transbutadiene[16] and more recently in a series of ab initio H^v studies of π-electron systems.[12,13,29−33] Nevertheless, because the H^v approach employs a number of approximations uncommon to traditional ab initio theory, it is instructive to review some of the specific choices and approximations used to construct the ab initio H^v π-electron parameters for the small, protonated Schiff base polyenes.

The ab initio H^v theory is based on Rayleigh−Schrödinger multireference-configuration many-body perturbation theory,[15] and, as such, describing the H^v calculations requires specifying the zeroth-order Hamiltonian H_0 employed in the present calculations. A well-chosen H_0 yields a well-converging perturbation series and thus physically meaningful results. A poor choice dooms the calculations. In fact, the third-order H^v theory is very robust with respect to the choice of the orbitals and orbital energies, but care must be taken to follow the general guidelines laid out in the original formulation by Freed and Sheppard[15] for choosing the zeroth-order orbitals and orbital energies.

Because we seek to derive semiempirical π-electron parameters from H^v calculations, the four zeroth-order atomic valence orbitals are constrained to be symmetry-adapted linear combinations of atomic $2p_\pi$ orbitals.[33] The atomic $2p_\pi$ orbitals are arbitrarily defined within the primitive ab initio basis, the Dunning PVDZ correlation consistent basis set,[41] as the first $2p_\pi$ contraction on each atom C and N.

No attempt has been made to optimize the atomic $2p_\pi$ orbitals because the precise choice of the atomic $2p_\pi$ orbitals does not affect the accuracy of the third-order H^v calculations, as demonstrated previously on hexatriene.[32] If one desires optimal atomic $2p_\pi$ orbitals, it would seem most convenient to choose the $2p_\pi$ orbital in order to minimize the third-order correlation contributions to the one-electron, two-center ($H_{u,v}$) effective integral because such a choice would simply comparisons to semiempirical theory.

Given the valence orbitals, the core orbitals are defined in the usual prescription[29−33] by performing a constrained ground-state SCF calculations in which the valence orbitals are not permitted to mix with the core or excited orbitals. This procedure allows the ab initio core to relax in the presence of the valence electrons, hopefully improving the convergence of the perturbation expansion. Likewise, the valence molecular orbitals mix among themselves, hopefully yielding a more convergent series. The core orbital energies are then taken as the diagonal matrix elements of the ground-state Fock matrix. The excited orbitals are then chosen by diagonalizing the N-1 electron ground-state Fock matrix, and the orbital energies are taken as the diagonal matrix elements of this operator.

These choices of the core and excited orbitals as well as the orbital energies are somewhat arbitrary, and, as above, the third-order calculations are not sensitive to the exact choices. This particular systematic choice, however, yields reasonable convergence for many polyenes because it seems to balance the terms in the numerators and denominators in the perturbation series. The orbital energies set the scale of the denominators, and the orbitals themselves are reflected matrix elements of the perturbation (V) that appear in the numerator. One can imagine other choices, such as using canonical HF orbitals and orbital energies for the excited orbitals. In such a case, one would find that the excited orbitals are very high, and, consequently, the energy denominators would be so large that the terms in the perturbation expansion would all be very small. Likewise, one could choose so-called “bare” core orbitals,[15] which correspond to HF orbitals for the polyenes containing zero π-electrons. The bare core orbitals make many of the terms in the numerator identically zero. Again, one would find that the core orbital energies are simply so low that the energy denominators are enormous and the perturbation theory would never converge. Again, no attempt has been made to optimize the choices of the core and excited orbitals or the orbital energies beyond the simple physical arguments given above. If one desires optimal core and excited orbitals, it might seem reasonable to adjust the orbitals and orbital energies such that the second-order calculations converge more rapidly.

For example, the current second-order calculations systematically overestimate the correlation contributions to the effective π-electron Coulomb interactions $G_{u,u}$ for all polyenes, and, consequently, $G_{u,u}$ oscillates strongly between first-, second-, and third-order. An improved choice of the core and excited orbitals (or orbital energies) might damp these oscillations at low order in the perturbation series, thus providing more accurate second-order effective interactions. One approach might simply rescale the orbital energies. Another would be to try using constrained core orbitals derived from a different SCF or MCSCF reference state, or even state-averaged MCSCF calculations.

All that now remains to completely specify H_0 is to define the valence orbital energies. This final step is quite simple but also most crucial in order to ensure practical convergence of the perturbation series. In all H^v calculations, the valence orbital energies are all given an average value, thus forcing the system to be quasi-degenerate. The corrections to this energy averaging arise in the numerator of the third-order perturbation theory. The conceptually simplest choice for an average orbital energy is to place the valence orbitals halfway between the highest core and lowest excited orbital (note that the lowest excited orbital is usually near zero). In the current calculations, we utilize a different procedure,[29−30,33] which places the valence orbitals at −0.42 au, slightly below the halfway energy of −0.32 au. The exact value is not critical, but it is important to use an average value. Indeed, the orbital averaging can convert a poorly diverging H^v calculation into a convergence or asymptotically convergent series, even in cases where the quasi-degeneracy conditions severely break down.[42,43]

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