

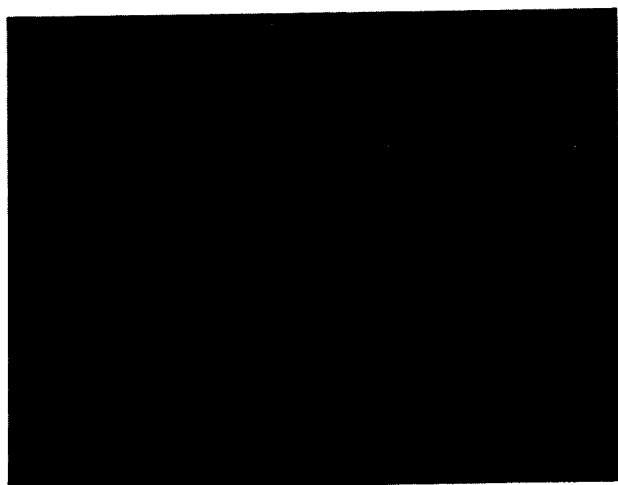


Figure 5. Optical texture of the chiral CuPc **2a** at 100°C (X300).

1b) suggest that the chiral PCH₂ **1a** could be a true disc-like cholesteric liquid crystal.

In the case of the chiral CuPc **2a**, however, an anisotropic phase began to appear at 187°C, showing the texture similar to small "fan-shape" texture in mesophase ranges (Figure 5). It should be pointed out that this was the only case in which the optical textures of CuPc's were different from those of the corresponding PCH₂'s reported in literatures so far.⁹ This result could be regarded as another evidence that the chiral PCH₂ **1a** is a columnar liquid crystal exhibiting cholesteric phase. It has been known by X-ray studies that the mean stacking distances of known discogenic Pc derivatives were about 4.6 ± 0.2 and 3.4 Å (characteristic van der Waals distance for aromatic compounds) for PCH₂ and CuPc, respectively.^{4,10,11} From these values it can be assumed that the chiral CuPc **2a** is difficult to form a "helical structure", but the columnar structure may be "tilted" due to interatomic

repulsions of the side chains.

Conclusion

From the results of the differences in the transition behaviors and the optical textures generated by chiral effect, i.e., a cholesteric-like texture (from platelet to fan-shape) of the chiral PCH₂ **1a**, and the difference in optical textures of the chiral PCH₂ **1a** and CuPc **2a**, the PCH₂ **1a** can be regarded as the first true columnar cholesteric phase displayed by the discotic liquid crystal systems.

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Dipole Moments of the OH, OH⁺ and OH⁻ Valence States by *ab initio* Effective Valence Shell Hamiltonian Method

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The *ab initio* effective valence shell Hamiltonian method, based on quasidegenerate many-body perturbation theory, is generalized to calculate molecular properties as well as the valence state energies which have previously been determined for atoms and small molecules. The procedure requires the evaluation of effective operator for each molecular property. Effective operators are perturbatively expanded in powers of correlation and contain contributions from excitations outside of the multireference valence space. To demonstrate the validity of this method, calculations for dipole moments of several low lying valence states of OH, OH⁺ and OH⁻ to first order in the correlations have been performed and compared with configuration interaction calculations.

Introduction

The quasidegenerate many-body perturbation theory (QDMBPT) is a generalization to multiple reference quaside-

generate states of simple many-body perturbation theory (MBPT), a diagrammatic representation of ordinary Rayleigh-Schrödinger perturbation theory for a reference nondegenerate single determinantal unperturbed wavefunction.¹⁻⁵

Whereas single reference state MBPT has been widely used to evaluate molecular properties, the QDMBPT formalism has rarely been applied to treat correlation effects on molecular properties for states that are represented in terms of many zeroth order reference configurations.⁶⁻⁹

Brandow and others have presented formal diagrammatic derivations of effective operators for properties, but no calculations have been presented except for simple atomic systems where the eigenfunctions are determined purely by symmetry, and, therefore, the approach in this atomic case reduces to one similar to that applied in MBPT.^{4,5} Very recently the effective valence shell Hamiltonian method (H^v) has been generalized to calculate molecular properties as well as the valence state energies.^{10,11} This H^v method is a multireference state perturbation formalism for treating electron correlations, and is based on QDMBPT. The H^v approach has been applied to a number of atomic and molecular systems where the computations of valence state energies show that the method provides an accurate description of the electronic structure. As for molecular properties, dipole moments and transition moments of the CH molecule are the only system studied using the H^v so far.¹²⁻¹⁶

In the H^v method, effective operators are required as an intermediate step and the expectation values are the diagonal matrix elements of the effective operators. The effective operators act only in the space by a set of valence orbitals, and the effective operators are defined in terms of perturbation sums over a complete set of complementary core and excited orbitals. The computation of correlated diagonal or off-diagonal matrix elements of the operator (A) proceeds first by determining the eigenfunctions of H^v and then by forming the matrix elements of effective operative operator (A^v) between these eigenfunctions. The diagonal and off-diagonal matrix elements of a given A^v can be obtained simultaneously for all valence states of a molecule and its ions.

Semiempirical electronic structure methods often consider molecular properties. The semiempirical model Hamiltonians are introduced based on chemical intuition and are parameterized to make computed energies and properties be in reasonable agreement with the experimental data. Certainly in semiempirical approach, the effective operators are considered like in the effective valence shell Hamiltonian H^v method. The difference is that the matrix elements of the effective operators are obtained from experimental data in semiempirical theory, but they are computed from first principles in H^v theory. So we see that the H^v has a dual purpose. One is that the practical computations of ab initio H^v can provide fundamental understandings for semiempirical methods and the other is H^v can be a new good ab initio method.

In the present paper, considerable interests are given to an ab initio aspect of H^v , i.e., H^v as a QDMBPT. As mentioned before, since the applications of QDMBPT to molecular properties have rarely been performed, it is of importance to compute the matrix elements of H^v , i.e., expectation values of A^v for various molecular systems. These applications will help one to assess the accuracy of QDMBPT.

For testing system, dipole moments of the OH molecule are chosen because OH is small enough to carry out computations without much efforts and the dipole moment is often sensitive enough to determine the accuracy of ab initio method. The outline of perturbative definition of the H^v for

properties is presented in section II and the computational details are described in section III. Section IV discusses the computational results.

Theory

Perturbation theory decomposes the molecular electronic Hamiltonian H into a zeroth order part H_0 and a perturbation V ,

$$H = H_0 + V \quad (1)$$

When H_0 is constructed as a sum of one-electron Fock Operators, then the perturbation V contains what we call the correlation corrections. The full many-electron Hilbert space can be divided into a primary space with projector P_0 and its orthogonal complement with projector $Q_0 = 1 - P_0$. The P_0 space is supposedly taken to contain a set of many-electron basis functions which are quasidegenerate with respect to the zeroth order Hamiltonian H_0 . Our choice below for P_0 takes it to span the valence space of all distinct configuration state functions involving a filled core and the remaining electrons distributed among the valence orbitals. Hence, the Q_0 space contains all basis functions with at least one core hole and/or one occupied excited orbital.

Quasidegenerate perturbation theory transforms the full Schrödinger equation

$$H\phi_i = E\phi_i \quad (2)$$

into the P_0 space effective valence shell Schrödinger equation

$$H^v\phi_i^v = E\phi_i^v \quad (3)$$

for the projection $\phi_i^v = P_0\phi_i$ where the E are the exact eigenvalues of (2). Several different perturbation expansions exist for H^v , but we choose to consider only Hermitian forms. Then, quasidegenerate perturbation theory gives the unique lowest order approximation¹

$$H^v = P_0 H P_0 + (1/2) \sum_{A, A'} P_0(A) V Q_0 (E_A - H_0)^{-1} Q_0 V P_0(A') + h.c. \quad (4)$$

where $h.c.$ designates the Hermitian conjugate of the preceding term and $P_0(A)$ designates the projector onto the valence space basis function $|A\rangle$.

Now consider an operator A whose diagonal and off-diagonal matrix elements between the normalized full space ϕ_i we desire. The matrix elements $\langle \phi_i | A | \phi_j \rangle$ may be transformed with quasidegenerate perturbation theory into the matrix elements of an effective valence shell operator A^v between the orthonormal valence space eigenfunctions ϕ_i^v ,

$$\langle \phi_i | A | \phi_j \rangle \equiv \langle \phi_i^v | A^v | \phi_j^v \rangle. \quad (5)$$

Again, the specification that A^v be Hermitian and independent of the state ϕ_i leads to the lowest nontrivial order perturbative expansion^{4,5,10,11}

$$A^v = P_0 A P_0 + \sum_{A, A'} P_0(A) V Q_0 (E_A - H_0)^{-1} Q_0 A P_0(A') + h.c. \quad (6)$$

Thus, we may obtain the expectation values and transition moments by first solving (3) and then by taking the corresponding matrix elements on the right hand side of (5). Once this A^v is obtained, it provides all diagonal and off-diagonal matrix elements, regardless of a number of valence electrons, in the P_0 space.

Either direct algebraic methods or many-body theory techniques can be used to reduce (6) to expressions for the matrix elements of A^v in the valence orbital basis. The resulting equations are summarized in the Appendix of Ref. 11 in terms of the core, one, two, ... body valence shell operators $A_c^v, A_1^v, A_2^v, A_3^v, \dots$, respectively, in the operator representation

$$A^v = A_c^v + \sum_i A_i^v + (1/2) \sum_{i,j} A_{ij}^v + \dots \quad (7)$$

where A_c^v is the constant contribution from the core, A_i^v is a one-electron operator with matrix elements $\langle v | A_i^v | v' \rangle$ in the valence orbital basis $\{v\}$, etc. The original full space operator A may have one and two-electron contributions, but here we consider only the dipole operator, so the A is one-electron operator.

When the operator A is a dipole operator, A^v is an effective dipole operator within the P_o space, i.e., the valence space. Though the dipole operator is a one-electron operator, the two-electron term, i.e., A_{ij}^v appears in the nontrivial lowest order A^v perturbation expansion. This two-electron term may look unrealistic, but this nonclassical term is necessary to obtain sensible ab initio H^v computational results.

The whole perturbation procedure is completely specified once the orbital basis and H_o are chosen. Diagonalization of the perturbative H^v in the P_o valence space yields the valence state energies and eigenfunctions ψ_i^v . The latter may then be employed along with (5) to calculate the expectation values and transition moments of some operator A by use of the effective valence shell operator A^v .

Calculations

The dipole operator in atomic units is defined as

$$\mu = \sum_a R_a Z_a + r \quad (8)$$

where Z_a is the charge on the nucleus a at the position R_a , and r is the position operator for all electrons, $r = \sum_i r_i$. Within the Born-Oppenheimer approximation the nuclear contribution $\sum_a R_a Z_a$ is a constant for a given molecular geometry, and it is only necessary to evaluate the diagonal and off-diagonal matrix elements of the electronic position operator r . For correspondence with the equations in section II, we merely replace $A \rightarrow r$, with the matrix elements $A_{ij} = \langle \phi_i | r | \phi_j \rangle$ written in terms of spinorbitals ϕ_i and ϕ_j for electron 1.

The definition of H_o specifies the computation of H^v and all effective property operators A^v . The eigenfunctions ψ_i^v of the second order H^v are used to evaluate the diagonal and off-diagonal matrix elements of the effective electronic position operator r^v . As mentioned before, though r is one-electron operator, in the effective form of r^v , two-electron terms (r_{ij}^v) must exist and have been computed.

Dipole moments of the OH molecule are chosen for the test application because there have been extensive computations of OH properties using configuration interaction (CI) type wavefunctions.¹⁷⁻²⁴ In the present calculations, the P_o space is the valence space of OH which consists of $2\sigma, 3\sigma, 1\pi$ and 4σ molecular orbitals. The 1σ orbital is taken as the core, and the all remaining orbitals lie in the excited space. The zeroth order Hamiltonian H_o is constructed as a diagonal in molecular orbital basis. The diagonal elements of H_o are called

Table 1. The Vertical Excitation Energies (eV) of OH and OH⁺. Ionization Potential (I.P.) and Electron Affinity (E.A.) of OH are also presented. The Internuclear Distance is 1.85au.

State		H ^v		CI		EXPTL
		SCF	BARE			
OH	X ² π	----	----	----	----	----
	A ² Σ ⁺	4.39	4.31	4.17 ^a	4.07 ^b	4.34 ^c 4.05 ^h
	B ² Σ ⁺	12.08	12.76			11.08 ^c 8.65 ^h
	C ² Σ ⁺	19.49	19.66			11.09 ^h
OH ⁺	X ³ Σ ⁻	----	----	----		----
	a ¹ Δ	2.53	2.26			
	A ³ π	4.32	4.02	3.66 ^d		3.60 ⁱ
	b ¹ Σ ⁺	4.12	3.83	3.72 ^d		3.53 ⁱ
	1 ¹ π	6.66	6.29			
	I.P.	11.66	12.19	12.36 ^e		13.36 ^j
E.A.	2.19	1.69	1.80 ^f	1.76 ^g	1.83 ^k	

^aTe from Ref. 17. ^bRef. 23. ^cCI(Ref. 27) at R = 1.85au with the same basis set used in the present work. ^dRef. 28. ^eRef. 29. ^fMøller Plesset perturbation from Ref. 30. ^gMBPT from Ref. 31. ^hNonadiabatic values from Ref. 32 and 33. ⁱTe from Ref. 34. ^jcited from Ref. 18. ^kRef. 35, 36, and 37.

ed orbital energies. The choice of orbital energies is quite flexible. That is, we can choose any type of orbital energies as far as the choice does not make the H^v expansion diverge. In the present calculations, two types of orbital energies are chosen. One is the orbital energies from the OH X²π self-consistent field wavefunctions. For this case, H_o is an ordinary Hartree-Fock operator. The other is orbital energies coming from the OH⁺ SCF calculations. The former will be called SCF orbital energies and the latter the bare core orbital energies. The orbital energies for the valence orbitals are averaged. This averaging removes energy denominator problems and guarantees the quasidegeneracy of the valence space.²⁴

The basis set is taken as Dunning's contracted Gaussians (4s3p) plus two d polarization functions on oxygen and contracted Gaussians (2s) plus one p polarization function on hydrogen²⁵. This basis set is chosen because extensive CI calculations with this basis set have been reported.^{26,27} The internuclear distance is fixed at 1.85au, which is very close to the equilibrium bond length of the OH X²π state.

Molecular orbitals are taken from the OH X²π ground state SCF calculations. The matrix elements of core (r_o^v), one-electron (r_i^v) and two-electron (r_{ij}^v) are all computed. The effective wavefunctions ψ_i^v are determined from the second order H^v calculations. Finally dipole moments, i.e., $\langle \psi_i^v | r^v | \psi_j^v \rangle$ are computed with the matrix elements of r^v for the several low-lying valence states of OH, OH⁺ and OH⁻ simultaneously.

Results and Discussion

To evaluate dipole moments we have first to obtain effective wavefunctions and, in the process of determining effective wavefunctions, energies of the valence states are also obtained. Table 1 displays the excitation energies of the several valence states for OH and OH⁺. Table 1 shows that our H^v excitation energies are in good agreement with other ab initio and experimental values. The two types of H^v calculations.

Table 2. Calculated Matrix Elements of Effective Dipole Operator for OH in au.

Matrix Element	H^v		Hartree-Fock
	SCF	BARE	
r_c^v	-0.000375	-0.000370	-0.000306
$\langle 2\sigma r_1^v 2\sigma \rangle$	-0.188648	-0.264865	-0.327365
$\langle 3\sigma r_1^v 3\sigma \rangle$	0.031212	-0.118395	-0.159425
$\langle 1\pi_x r_1^v 1\pi_x \rangle$	0.018869	-0.040685	-0.055278
$\langle 4\sigma r_1^v 4\sigma \rangle$	-2.817310	-1.390968	-1.280121
$\langle 2\sigma r_1^v 3\sigma \rangle$	0.133277	0.489726	0.773137
$\langle 2\sigma r_1^v 4\sigma \rangle$	-0.444512	0.219238	-0.650798
$\langle 3\sigma r_1^v 4\sigma \rangle$	-0.977790	-0.689990	-0.444154
$\langle 2\sigma r_1^v 1\pi_x \rangle$	-0.248767	-0.366822	-0.650798
$\langle 3\sigma r_1^v 1\pi_x \rangle$	-0.087138	-0.050382	-0.139895
$\langle 4\sigma r_1^v 1\pi_x \rangle$	-0.129845	-0.030326	0.082452
$\langle 2\sigma 2\sigma r_{12}^v 2\sigma 2\sigma \rangle$	-0.059091	-0.027758	
$\langle 3\sigma 3\sigma r_{12}^v 3\sigma 3\sigma \rangle$	-0.037525	-0.010131	
$\langle 4\sigma 4\sigma r_{12}^v 4\sigma 4\sigma \rangle$	0.610530	0.228554	
$\langle 1\pi_x 1\pi_x r_{12}^v 1\pi_x 1\pi_x \rangle$	-0.043925	-0.015654	
$\langle 3\sigma 2\sigma r_{12}^v 3\sigma 2\sigma \rangle$	-0.012849	0.011757	
$\langle 4\sigma 2\sigma r_{12}^v 4\sigma 2\sigma \rangle$	0.291086	0.023463	
$\langle 4\sigma 3\sigma r_{12}^v 4\sigma 3\sigma \rangle$	0.304252	0.046068	
$\langle 1\pi_x 2\sigma r_{12}^v 1\pi_x 2\sigma \rangle$	-0.024183	-0.001693	
$\langle 1\pi_x 3\sigma r_{12}^v 1\pi_x 3\sigma \rangle$	-0.070997	-0.026789	
$\langle 1\pi_x 4\sigma r_{12}^v 1\pi_x 4\sigma \rangle$	0.225888	0.014258	
$\langle 1\pi_y 1\pi_x r_{12}^v 1\pi_y 1\pi_x \rangle$	-0.038368	-0.013643	
$\langle 3\sigma 2\sigma r_{12}^v 2\sigma 3\sigma \rangle$	-0.053417	0.028132	
$\langle 4\sigma 2\sigma r_{12}^v 2\sigma 4\sigma \rangle$	-0.042572	-0.011807	
$\langle 4\sigma 3\sigma r_{12}^v 3\sigma 4\sigma \rangle$	0.041108	-0.010739	
$\langle 1\pi_x 2\sigma r_{12}^v 2\sigma 1\pi_x \rangle$	-0.000426	0.004352	
$\langle 1\pi_x 3\sigma r_{12}^v 3\sigma 1\pi_x \rangle$	-0.008862	-0.007420	
$\langle 1\pi_x 4\sigma r_{12}^v 4\sigma 1\pi_x \rangle$	0.015295	0.000102	
$\langle 1\pi_y 1\pi_x r_{12}^v 1\pi_x 1\pi_y \rangle$	-0.002779	-0.001006	

Table 3. Dipole Moments(au) of OH, OH⁺ and OH⁻ at the Internuclear Distance of 1.85au.

State	H^v		CI	EXPTL
	SCF	BARE		
OH X ² π	0.6440	0.6763	0.6442 ^a 0.6493 ^b 0.6589 ^c 0.6768 ^d 0.6621 ^d 0.6617 ^e	
A ² Σ^+	0.6855	0.7334	0.6804 ^a	
B ² Σ^+	-0.3115	-0.3170		
C ² Σ^+	0.3756	0.5363		
OH ⁺ X ³ Σ^-	1.0250	0.9626	0.9015 ^b	
a ¹ Δ	1.0343	0.9663		
A ³ π	0.9723	0.9245		
b ¹ Σ^+	1.0144	0.9482		
1 ¹ π	1.0033	0.9909		
OH ⁻ X ¹ Σ^+	0.3542	0.3711	0.4147 ^b	

^aRef. 17. ^bCoupled electron pair approximation(CEPA) from Ref. 38. OH (R = 1.837au), OH⁺ (R = 1.946au) and OH⁻ (R = 1.825au). ^cOptimized valence configuration calculations from Ref. 19. (R = 1.8342au). ^dCEPA from Ref. 39 (R = 1.83au). ^eCI from Ref. 26 at R = 1.85au with the same basis set used in the present paper. ^fRef. 40.

SCF and BARE values are close to each other and it verifies that the second order H^v is accurate enough. For the B² Σ^+ and C² Σ^+ states, our H^v excitation energies appear to be wrong when they are compared with experimental values. Our values are vertical excitation energies, but experimental ones are nonadiabatic values. The potential minimum of B and C² Σ^+ states are far from the 1.85au which is about the equilibrium bond length of the X² π state.

The nuclear contribution to the dipole moment is 1.85au, because the internuclear distance of the OH molecule is fixed at 1.85au. The positive sign of the dipole moment is defined as the polarity of O ^{δ^-} H ^{δ^+} . The origin of the coordinate is chosen at the oxygen atom.

Table 2 shows the matrix elements of the one- and two-electron parts of r^v in the valence orbital basis. The core part $r_c^v = \langle 1\sigma | r_1^v | 1\sigma \rangle$ is very small, but the H^v value is different from the Hartree-Fock value. The Hartree-Fock values are expectation values of r operator between SCF molecular orbitals. The difference represents a contribution from core correlation to the dipole moment. Thus, core-core and core-valence correlations contribute to the dipole moment and must be considered. Table 2 also shows that one-electron matrix elements are larger than the two-electron ones. The two-electron matrix elements which do not exist in the original dipole operator are small, but can not be neglected.

The total dipole moment, μ^v is a sum of the nuclear part (1.85au) and the electronic part(r^v). The electronic part is an expectation value of r^v of the valence state. As noted before, a unique feature of the H^v method is the fact that all valence state energies and properties are obtained simultaneously for the neutral molecule and its ions from a single computation of H^v and A^v . Table 3 shows the H^v total dipole moments for several valence states of OH, OH⁺ and OH⁻. Other ab initio values are also listed for a comparison.

Table 3 displays two types of H^v calculations. The H^v dipole moments of these two types differ by less than 10% in magnitude. This discrepancy has been expected and, in a practical sense, it justifies that the lowest order A^v expansion is a reasonable approximation to an exact infinite order perturbation expansion. The H^v values are in good agreement with other ab initio values. The small discrepancy is due to the different sizes of basis set and the different internuclear distance considered in various calculations. The footnote in Table 3 explains it in detail.

The effective valence shell Hamiltonian formalism has been extended to treat operators for properties and transition moments other than the effective Hamiltonian for the valence state energies. The lowest order correlation corrections for the effective operators is analyzed for molecular properties corresponding to one-electron operators, and explicit computations are presented for the dipole moments for several low lying electronic states of the OH, OH⁺ and OH⁻ molecules at the OH ground state equilibrium position.

Our computed dipole moments are in reasonable agreement with configuration interaction calculations of the same quantities that have been made using considerably larger basis sets, and this comparison supports the utility of the effective Hamiltonian method for molecular properties. Additional questions involve the convergence of calculated properties as a function of the basis set size and the contributions of higher order corrections in the perturbation expansion for the

effective operators A^v . The latter question is a very difficult one to answer at present because the next order corrections involve several hundred diagrams¹⁰ and, therefore, a rather lengthy programming problem. However, experience with the corresponding order corrections to energy calculations¹²⁻¹⁶ show these higher order energy contributions often to be fairly small. The two-electron matrix elements are small, but significant, and it is clear that semiempirical theories with only one-electron dipole operators must effectively be averaging these two-electron contributions into their semiempirical procedure.

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