

RELATIVISTIC MULTICONFIGURATION TIME-DEPENDENT SELF-CONSISTENT-FIELD THEORY FOR MOLECULES

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A relativistic multiconfiguration time-dependent self-consistent-field theory is constructed for molecules. Equations are derived for relativistic response functions, and their solutions are found in general form for multielectron molecules. Within the adopted approach, the equivalence of the results of relativistic calculations of the oscillator strengths in the molecules is demonstrated by using equations in "length" and "velocity." A relativistic formalism is formulated for the Liouville-Dirac-Fock self-consistent field; this formalism may be very effective in molecular calculations.

One pressing task for modern molecular theory is to develop consistent relativistic methods of molecular calculations (see, e.g., [1]). This is due to a number of factors, particularly the fact that accurate calculations of heavy and superheavy molecular systems require allowance for relativistic effects in addition to correlation effects. An adequate description of the characteristics of chemical bonding in a number of compounds of d and f elements, particularly oxides of lanthanides and actinides (see [2]), is possible only when relativistic interactions, specifically spin-orbit interactions, are taken into consideration. In recent years a number of relativistic versions of well-known nonrelativistic quantum chemical methods have been developed: among the semiempirical methods are the method of the relativistic model potential, the relativistic X_α method, and others, and among the nonempirical methods are the relativistic one-configuration Hartree-Fock (HF) method, the Dirac-Fock (DF) method, and others (see [3-7]). However, the specific application of most of these methods of molecular calculations entails a number of both computational and theoretical problems. For instance, proper handling of relativistic operators requires the use of the bases of the relativistic orbitals, which are considerably larger in volume than in the corresponding nonrelativistic versions. Correlation effects must be taken into account accurately in consistent molecular calculations. As we know, the one-configuration Hartree-Fock and Dirac-Fock self-consistent-field methods do not take into account the correlation, and moreover the one-configuration wave function does not make it possible to obtain the correct dissociation limit. The recently formulated multiconfiguration Dirac-Fock self-consistent-field method [8] has not come into use in molecular calculations because of the still essentially insurmountable computational difficulties, although in light of recent achievements that improve optimization techniques [9] and of course progress in computational technology, it remains an extremely promising method of relativistic quantum chemistry. The same also applies to the time-dependent counterparts of the method. The purpose of this paper is to formulate the relativistic multiconfiguration time-dependent (TD) formalism of the Dirac-Fock self-consistent field for molecules, which generalizes the corresponding multiconfiguration Hartree-Fock formalism. Moreover, this paper offers a new nonempirical approach to molecular calculation, the Liouville-Dirac-Fock method, which has a number of advantages over other traditional a priori methods. The literature contains a fairly large number of formulations of time-dependent nonrelativistic theories, particularly time-dependent one-configuration and multiconfiguration Hartree-Fock theories, the random-phase approximation, the method of linearized equations of motion for electron-hole excitations, the moment expansion of the polarization propagator, and generalizations of these theories (see, e.g., [10, 11]). These approaches are essentially nothing but in some sense equivalent formulations of linear response theory for multielectron molecules. Of course, the relativistic formulation has its own peculiarities.

TEMPORAL VARIATIONS OF THE DIRAC-FOCK
MULTICONFIGURATION WAVE FUNCTION

To consider the temporal variations of the multiconfiguration Dirac-Fock wave function $\psi(t)$, we use the Frenkel variational principle in the form [12]

$$\text{Re} \langle \delta \Psi \left| i \frac{\partial}{\partial t} - H \right| \Psi \rangle = 0. \quad (1)$$

The wave function in the multiconfiguration Dirac-Fock theory is expressed in terms of the expansion in configuration functions with expansion coefficients C_i :

$$|0\rangle = \sum_i |\Phi_i\rangle C_i. \quad (2)$$

The functions Φ_i are formed by a minimal number of Slater determinants from the one-electron molecular spinors (MS's) $\{\varphi_i\}$ so that the symmetry requirements of the wave function are observed. It is assumed that the MS's form the orthogonal system

$$\langle \varphi_i | \varphi_j \rangle = \delta(i, j).$$

Each MS has the form

$$\varphi_i = \begin{pmatrix} \varphi_{i1} \\ \varphi_{i2} \\ \varphi_{i3} \\ \varphi_{i4} \end{pmatrix} \quad (3)$$

and in the Roothaan expansion method is represented as a linear combination of atomic spinors χ_p centered on different atoms of the molecular system:

$$\varphi_i = \sum_{p=1}^m \chi_p C_{pi}, \quad (4)$$

where χ_p is a four-component atomic spinor. The condition of orthonormality is $\sum_{pq} C_{pi}^* S_{pq} C_{qj} = \delta(i, j)$, where $S_{pq} = \langle \chi_p | \chi_q \rangle$ is the overlap integral. Now let an external perturbation in the form

$$W(t) = (V e^{-i\omega t} + V^+ e^{i\omega t}) e^{\eta t}, \quad (\eta > 0), \quad (5)$$

which corresponds to adiabatic inclusion, be applied to the molecular system. We introduce the following expression as the ansatz for the bispinor $|\psi(t)\rangle$:

$$|\psi(t)\rangle = \begin{pmatrix} e^{i\hat{\Lambda}} & 0 \\ 0 & e^{i\hat{\Omega}} \end{pmatrix} \begin{pmatrix} e^{i\hat{K}} & 0 \\ 0 & e^{i\hat{L}} \end{pmatrix} |0\rangle e^{-iEt}, \quad (6)$$

where $\hat{\Lambda}$, \hat{K} , $\hat{\Omega}$, and \hat{L} are Hermitian operators that generate transformations of the wave-function components and the correlation coefficients C_i in Eq. (1). According to [11], $\hat{\Lambda}$ and \hat{K} may be represented as

$$\hat{\Lambda} = \sum_{r>s} (\Lambda_{rs} a_r^+ a_s + \Lambda_{rs}^+ a_s^+ a_r) = \sum_v (\Lambda_v q_v^+ + \Lambda_v^+ q_v); \quad (7)$$

$$\hat{K} = \sum_n (|n\rangle d_n \langle 0| + |0\rangle d_n^* \langle n|) = \sum_n (d_n \kappa_n^+ + d_n^* \kappa_n), \quad (8)$$

where a^+ and a are the electron creation and annihilation operators, and $|n\rangle$ is defined as

$$|n\rangle = \sum_i |\Phi_i\rangle C_{in}, \quad C^+ C = 1 \quad (9)$$

and forms an orthogonal supplement to the unperturbed state $|0\rangle$. The quantities Ω and L also

can be defined analogously. Variational principle (1) with $|\psi\rangle$ in the form of Eq. (6) then enables us to obtain the system of equations

$$\begin{aligned} i \langle [\delta\Lambda + \delta K, \dot{\Lambda} + \dot{K}] \rangle &= -i \langle [\delta\Lambda + \delta K, H] \rangle + \frac{1}{2} \delta \langle [\Lambda, [H, \Lambda]] \rangle + \\ &+ \langle [K, [H, K]] \rangle + \delta \langle [K, [H, \Lambda]] \rangle + \dots; \\ i \langle [\delta\Omega + \delta L, \dot{\Omega} + \dot{L}] \rangle &= -i \langle [\delta\Omega + \delta L, H] \rangle + \frac{1}{2} \delta \langle [\Omega, [H, \Omega]] \rangle + \\ &+ \langle [L, [H, L]] \rangle + \delta \langle [L, [H, \Omega]] \rangle + \dots \end{aligned} \quad (10)$$

If we hereafter write the total Hamiltonian as the sum of the unperturbed part H_0 and the perturbations $W(t)$, where $H = H_0 + W(t)$, and using the generalized Brillouin theory $\langle [\delta\Lambda + \delta K, H_0] \rangle = 0$ and the identities

$$\begin{aligned} \delta \langle [\Lambda, [H_0, \Lambda]] \rangle &= 2 \langle [\delta\Lambda, [H_0, \Lambda]] \rangle, \\ \delta \langle [\Omega, [H_0, \Omega]] \rangle &= 2 \langle [\delta\Omega, [H_0, \Omega]] \rangle, \end{aligned} \quad (11)$$

in the linear response approximation, we obtain the following instead of Eq. (10):

$$\begin{aligned} i \langle [\delta\Lambda + \delta K, \dot{\Lambda} + \dot{K}] \rangle &= -i \langle [\delta\Lambda + \delta K, W(t)] \rangle + \\ &+ \langle [\delta\Lambda + \delta K, [H_0, \Lambda]] \rangle + \langle [[\delta\Lambda + \delta K, H_0], K] \rangle, \\ i \langle [\delta\Omega + \delta L, \dot{\Omega} + \dot{L}] \rangle &= -i \langle [\delta\Omega + \delta L, W(t)] \rangle + \\ &+ \langle [\delta\Omega + \delta L, [H_0, \Omega]] \rangle + \langle [[\delta\Omega + \delta L, H_0], L] \rangle. \end{aligned} \quad (12)$$

RELATIVISTIC RESPONSE FUNCTION FOR A MULTIELECTRON MOLECULE

In the linear response approximation with consideration for the type of operator W (5), the functions $\Lambda(t)$, $d(t)$, $\Omega(t)$, and $L(t)$ may be constructed in the form

$$\begin{aligned} \lambda_v(t) &= \alpha_{v1}(\omega) e^{-i(\omega+i\eta)t} + \beta_{v1}^*(\omega) e^{-i(-\omega+i\eta)t}; \\ d_n(t) &= \alpha_{n1}(\omega) e^{-i(\omega+i\eta)t} + \beta_{n1}^*(\omega) e^{-i(-\omega+i\eta)t}; \end{aligned} \quad (13)$$

$$\begin{aligned} \Omega_v(t) &= \alpha_{v2}(\omega) e^{-i(\omega+i\eta)t} + \beta_{v2}^*(\omega) e^{-i(-\omega+i\eta)t}; \\ L_n(t) &= \alpha_{n2}(\omega) e^{-i(\omega+i\eta)t} + \beta_{n2}^*(\omega) e^{-i(-\omega+i\eta)t}. \end{aligned} \quad (14)$$

With consideration for Eqs. (7)-(8), (13), and (14), Eq. (12) reduces to a linear system of equations for the quantities $\alpha_{v,n}$ and $\beta_{v,n}$. Introducing for convenience the following matrices by analogy with [11]

$$\begin{aligned} A_1 &= \begin{pmatrix} A & 0 \\ 0 & A \end{pmatrix}, \quad A = \begin{Bmatrix} \langle [q_v, H_0], q_v^+ \rangle & \langle [q_v, H_0], \kappa_n^+ \rangle \\ \langle [\kappa_n, H_0], q_v^+ \rangle & \langle [\kappa_n, H_0], \kappa_n^+ \rangle \end{Bmatrix}, \\ S_1 &= \begin{pmatrix} S & 0 \\ 0 & S \end{pmatrix}, \quad S = \begin{Bmatrix} \langle [q_v, q_v^+] \rangle & \langle [q_v, \kappa_n^+] \rangle \\ \langle [\kappa_n, q_v^+] \rangle & \langle [\kappa_n, \kappa_n^+] \rangle \end{Bmatrix}, \end{aligned}$$

as well as the matrices B_1 and Δ_1 , which are analogous to A_1 and S_1 , but with the difference that the operators q and k are adjoint, we write the sought system as

$$\left[(\omega + i\eta) \begin{pmatrix} S_1 & \Delta_1 \\ \Delta_1^+ & -S_1^* \end{pmatrix} - \begin{pmatrix} A_1 & B_1 \\ B_1^+ & A_1^* \end{pmatrix} \right] \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = -i \begin{pmatrix} V_1 \\ V_2 \end{pmatrix}, \quad (15)$$

where

$$\alpha = \begin{pmatrix} \alpha_{v1} \\ \alpha_{v2} \\ \alpha_{n1} \\ \alpha_{n2} \end{pmatrix}; \quad \beta = \begin{pmatrix} \beta_{v1} \\ \beta_{v2} \\ \beta_{n1} \\ \beta_{n2} \end{pmatrix}; \quad V_1 = \begin{pmatrix} \langle [q_v, V] \rangle \\ \langle [q_v, V] \rangle \\ \langle [\kappa_n, V] \rangle \\ \langle [\kappa_n, V] \rangle \end{pmatrix}; \quad V_2 = \begin{pmatrix} \langle [q_v^+, V] \rangle \\ \langle [q_v^+, V] \rangle \\ \langle [\kappa_n^+, V] \rangle \\ \langle [\kappa_n^+, V] \rangle \end{pmatrix}.$$

The solution of Eq. (15) now is found by using well-known standard methods (see, e.g., [11, 13]). In concluding this section, we will note that, as in the multiconfiguration Hartree-Fock theory, in the relativistic Dirac-Fock approach the different equivalent expressions for determining the oscillator strengths in molecules that are known to characterize the electron transitions in the absorption spectrum give the same result. The proof is almost entirely analogous to the proof in the multiconfiguration Hartree-Fock theory, but with the difference that relativistic propagators now are involved in our treatment and the matrix elements are selected on the bispinors $|0\rangle$, $|J\rangle$. The value of the oscillator strength of the molecule in the dipole approximation is given by the equations:

In the "length" approximation

$$f_{0J}^l = \frac{2}{3} (E_J - E_0) |\langle 0 | \hat{R} | J \rangle|^2$$

And in the "velocity" approximation

$$f_{0J}^v = \frac{2}{3} (E_J - E_0)^{-1} |\langle 0 | \hat{P} | J \rangle|^2.$$

Here \hat{R} and \hat{P} are respectively the dipole moment operator and the linear moment operator, which are related by the Heisenberg equation:

$$iP = [R, H_0].$$

The matrix elements from the operators \hat{R} and \hat{P} on the bispinors and hence f^l and f^v are related to the corresponding propagators by the equations

$$f_{0J}^l = \frac{2}{3} \omega_J \text{Res} [\text{Sp} \ll R, R \gg_E];$$

$$f_{0J}^v = \frac{2}{3} \omega_J^{-1} \text{Res} [\text{Sp} \ll P, P \gg_E],$$

where Res signifies the residue in the pole $\omega_J = (E_J - E_0)$. Then with consideration for the identity $E^2 \ll R, R \gg_E = \ll P, P \gg_E + i \ll [P, R] \gg$, we obtain $f_{0J}^l = f^v$.

LIUVILLE-DIRAC-FOCK FORMALISM IN THE THEORY OF MULTIELECTRON MOLECULES

Although, as we indicated above, the Dirac-Fock method is as before a promising ab initio method in molecular calculations; nonetheless, existing theoretical or computational difficulties limit the possibility of using it extensively. A method of calculating energies and transition probabilities that is based on a procedure for solving the Liouville equation was proposed recently in [14] as an alternative to the Dirac-Fock formalism for multiply charged ions and ionized atoms. The promise of this method in the sense of making allowance for correlation effects has been demonstrated through the example of a calculation of argon-like ions. We believe that this approach may prove especially effective in molecular theory as well. We shall present a derivation of the basic equations of Liouville-Dirac-Fock formalism for a multielectron molecule. The equation for the eigenvalues of the Liouville operator has the form

$$Lt = [H, t] = \lambda t, \quad (16)$$

where H is the Dirac multielectron Hamiltonian, which for a molecule has the form

$$H = \sum_i \left(c\alpha_i p_i + \beta c^2 - \sum_a \frac{Z_a}{r_{ia}} \right) + \sum_{i < j} \frac{1}{r_{ij}}$$

(all notations here are standard). Let the multiconfiguration wave functions for the initial and final states of the molecule that are a result of excitation, for example, be determined from expressions (2). Then the Liouville equations can be solved if we adopt the matrix elements in Eq. (16) on the functions of the initial and final states $|\psi_i\rangle$ and $|\psi_f\rangle$. As a result we have

$$\sum_{i, n} M_{in} \langle n | H | i \rangle = \lambda \sum_{i, n} M_{in} \langle n | t | i \rangle;$$

$$|\psi_i\rangle = \sum_{i=1}^{N_i} C_i |i\rangle, \quad |\psi_f\rangle = \sum_{n=1}^{N_f} C_n |n\rangle, \quad (17)$$

where $M_{in} = C_i C_n^*$. Taking into account

$$1 = \sum_m |m\rangle \langle m| + \sum_j |j\rangle \langle j|,$$

we may rewrite Eq. (17) in the form

$$\sum_{i, n, m} M_{in} \langle n | H | m \rangle \langle m | t | i \rangle - \sum_{inj} M_{in} \langle n | t | j \rangle \langle j | H | i \rangle =$$

$$= \lambda \sum_{i, n} M_{in} \langle n | t | i \rangle. \quad (18)$$

Then, regrouping the terms in Eq. (18), after the usual transformations we obtain

$$\sum_{i, n} [\sum_m M_{im} H_{mn} - \sum_j H_{ij} M_{jn} - \lambda M_{in}] t_{ni} = 0,$$

where $H_{ij} = \langle i | H | j \rangle$. As a result we obtain a system of $N_i N_f$ independent equations:

$$\sum_m M_{im} H_{mn} - \sum_j H_{ij} M_{jn} - \lambda M_{in} = 0$$

The solution of this system can be effected by using the usual self-consistent variational procedure, as in Dirac-Fock theory. Let us emphasize in conclusion that a calculation of the oscillator strengths using the wave functions calculated on the basis of the solution of Eq. (18) is gauge invariant. The problem is that, as in the case of atoms, the gauge-dependent part of the dipole transition operator in the case of a molecule has the form

$$G \left[\frac{a \nabla \Phi_{l\lambda}}{-i\lambda} + \Phi_{l\lambda} \right],$$

where $\Phi_{l\lambda}$ is the scalar potential ($\Phi_{l\lambda} \sim C_\lambda^{(1)}(\theta, \varphi)$), and moreover $\Phi_{l\lambda}$ satisfies the equation

$$\langle \psi_f | [H \Phi_{l\lambda}] | \psi_i \rangle = \lambda \langle \psi_f | \Phi_{l\lambda} | \psi_i \rangle.$$

By virtue of the validity of the relation

$$[H \Phi_{l\lambda}] = -i[a \nabla, \Phi_{l\lambda}] = -ia \nabla \Phi_{l\lambda}.$$

the gauge-dependent term may be written as

$$G \left[\frac{[H, \Phi_{l\lambda}]}{-\lambda} + \Phi_{l\lambda} \right]. \quad (19)$$

As one can see readily, matrix element (19) is canceled. Gauge invariance is observed in this case, primarily as a result of the completeness of the system of states in the commutators in Eq. (17), and also because ψ_i and ψ_f are the eigenfunctions of the operator H . Of course, in specific quantum-chemical calculations one must deal with limited bases (especially in relativistic calculations); in this case gauge invariance naturally will not be observed. At first glance this unhappy circumstance may prove quite useful for use in constructing optimized chemical bases. This question will be addressed in a separate paper.

LITERATURE CITED

1. G. Malli (ed.), *Relativistic Effects in Atoms, Molecules, and Solids*, NATO Advanced Study Institute, Vancouver (1981).
2. R. W. Field, *Ber. Bunsenges. Phys. Chem.*, 86, 771-779 (1982).
3. R. L. Martin, *J. Phys. Chem.*, 87, 750-754 (1978).
4. J. Johnson, *Semiempirical Methods of Calculating Electronic Structure* [Russian translation], Mir, Moscow (1978), pp. 139-174.
5. A. V. Glushkov, *Zh. Strukt. Khim.* 29, No. 4, 3-10 (1988).
6. G. Malli and J. Oreg, *J. Chem. Phys.*, 63, 830-837 (1975).
7. G. Malli, *Chem. Phys. Lett.*, 73, 510-513 (1980).
8. O. Matsuoka, N. Suzuki, T. Aoyama, and G. Malli, *J. Chem. Phys.*, 73, 1320-1329 (1980).
9. E. Dalgaard and P. Jorgensen, *J. Chem. Phys.*, 69, 3833-3839 (1978).
10. J. Oddershede, *Adv. Quantum Chem.*, 11, 275-321 (1978).
11. E. Dalgaard, *J. Chem. Phys.*, 72, 816-823 (1980).
12. P. W. Langhoff, S. T. Epstein, and M. Karplus, *Rev. Mod. Phys.*, 44, 602-654 (1972).
13. J. Linderberg and Y. Ohrn, *Int. J. Quantum Chem.*, 12, 161-174 (1977).
14. D. Frye and L. Armstrong, Jr., *Phys. Rev. A*, 31, 2070-2077 (1985).