

NOTIZEN

Solution of the Molecular Bethe-Goldstone Equation

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Recently a very efficient method for solving the Bethe-Goldstone equation was proposed¹. The main points are:

i) The Bethe-Goldstone wavefunction is constructed from eigenfunction of the two particle system without taking the Pauli operator into account.

ii) The solution of the Bethe-Goldstone equation is obtained by treating the Pauli operator exactly.

The reaction matrix G is defined as

$$G = V + V \frac{Q}{E - E_0} G \quad (1)$$

where V and Q are the perturbation and the Pauli operator respectively.

The perturbed wavefunction $\psi_a(\text{BG})$, known as the Bethe-Goldstone function, is obtained from

$$\langle \Phi_\beta | G | \Phi_\alpha \rangle = \langle \Phi_\beta | V | \psi_a(\text{BG}) \rangle = K_{\beta\alpha} \quad (2)$$

where Φ_β is an unperturbed two particle function.

With Eqs. (1) and (2) the $\psi_a(\text{BG})$ satisfies the equation:

$$\psi_a(\text{BG}) = \Phi_a + \sum_{\mu} \{ Q_{\mu} \Phi_{\mu} \langle \Phi_{\mu} | V | \psi_a(\text{BG}) \rangle / (E_a(\text{BG}) - \varepsilon_{\mu}) \}, \quad (3)$$

$$E_a(\text{BG}) = \varepsilon_a + \langle \Phi_a | V | \psi_a(\text{BG}) \rangle \quad (4)$$

where ε_a is the energy of the unperturbed function (Φ_a). Due to the faster convergence $\psi_a(\text{BG})$ is ex-

panded using a set of functions ψ_{γ}

$$\psi_a(\text{BG}) = \sum_{\gamma} a_{\gamma a} \psi_{\gamma} \quad (5)$$

where ψ_{γ} is a solution of

$$(H_0 + V) \psi_{\gamma} = E_{\gamma} \psi_{\gamma}. \quad (6)$$

The Bethe-Goldstone wavefunction can be deduced by using Eqs. (5) and (6) and with the self-consistent procedure using Eqs. (3) and (4).

The system we have studied was a molecule of trans-butadiene with four π -electrons. Equation (6) is solved by expanding ψ_{γ} into Hückel molecular orbitals (theoretical parameters from Ref. ²). The expansion has to be separated into singlet and triplet parts:

$$\psi_{\gamma}^{\text{s,t}} = \sum_{m,n} d_{mn\gamma} [\varphi_m(1) \varphi_n(2) \pm \varphi_m(2) \varphi_n(1)]$$

with d_{mn} determined from Equation (6).

Φ_a in Eq. (3) expands into Hückel molecular orbitals too:

$$\Phi_a^{\text{s,t}} = A [\varphi_m(1) \varphi_n(2) \pm \varphi_m(2) \varphi_n(1)].$$

The energy of the system is given by summing the pairs energies [Eq. (4)] using the values for singlets and triplets with appropriate weighting coefficients. The calculated electronic energy is $E = -93.267$ eV, while the SCF energy is -93.79 eV. The calculation resulted in an interesting result. It shows that the solution of the Bethe-Goldstone equation with its independent pair approximation gives almost the same result as the SCF method. One can then expect that the energy obtained from the Bethe-Goldstone method with the perturbation $1/r_{ij} - v_{\text{H.F.}}$, where $v_{\text{H.F.}}$ is the Hartree-Fock potential, approaches the true one³. Because of the separation of ψ_{γ} into singlet and triplet components it is possible to separate E into these parts too. The singlet part constitutes 89% of E and the triplet 11%.

These are interesting results that show that the triplet contribution is significant. Within the singlet contribution the pairs (ii) contribute 71% and the pairs (ij) 29%.

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¹ J. S. TRUELOVE and I. R. NICHOLS, Aust. J. Phys. **23**, 231 [1970]. — B. R. BARRET, R. C. L. HEWITT, and R. J. MC CARTHY, Phys. Rev. C **2**, 1199 [1970].

² V. STAEMMLER and W. KUTZELNIGG, Theor. Chim. Acta **9**, 67 [1967].

³ R. K. NESBET, T. L. BARR, and E. R. DAVIDSON, Chem. Phys. Lett. **4**, 203 [1969].



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