NOTIZEN

Solution of the Molecular Bethe-Goldstone Equation

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Recently a very efficient method for solving the Bethe-Goldstone equation was proposed[1]. 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

$$G = V + V \frac{Q}{E - E_0} G \tag{1}$$

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

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

$$\langle \Phi_\beta \mid G \mid \Phi_a \rangle = \langle \Phi_\beta \mid V \mid \psi_a(\mathrm{BG}) \rangle = K_{\beta a} \tag{2}$$

where Φ_β is an unperturbed two particle function.

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

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

$$E_a(\mathrm{BG}) = \varepsilon_a + \langle \Phi_a \mid V \mid \psi_a(\mathrm{BG}) \rangle \tag{4}$$

where ε_a is the energy of the unperturbed function (Φ_a). Due to the faster convergence $\psi_a(\mathrm{BG})$ is expanded using a set of functions ψ_γ

$$\psi_a(\mathrm{BG}) = \sum_\gamma a_{\gamma a} \, \psi_\gamma \tag{5}$$

where ψ_γ is a solution of

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

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:

$$\psi_\gamma^{\mathrm{S{\cdot}T}} = \sum_{m,n} d_{mn\gamma} \, [\varphi_m(1) \, \varphi_n(2) \pm \varphi_m(2) \, \varphi_n(1)]$$

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

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

$$\Phi_\alpha^{\mathrm{S,T}} = A [\varphi_m(1) \, \varphi_n(2) \pm \varphi_m(2) \, \varphi_n(1)] \, .$$

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 $1/r_{ij} - v_{\mathrm{H.F.}}$, where $v_{\mathrm{H.F.}}$ is the Hartree-Fock potential, approaches the true one[3]. 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 constitues 89% of E an 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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