

π 和 σ 体系彻底分离的高度定域的键轨道基组的建立

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摘要 高度定域的、对称的、键轨道基组的建立是一个多步的计算程序: (1)以定域片断轨道 $[\phi_k, \phi_i, \phi_j]$ 为基,对分子作有条件的RHF运算,算得FUL和DSI $^\circ$ 态的片断分子轨道 $[\Phi^{\circ}l, \Phi^{\circ}n, \Phi^{\circ}m]$ 和 $[\Phi_l, \Phi_n, \Phi_m]$ 。在基组 $[\phi_k, \phi_i, \phi_j]$ 中, $\phi_i \in$ 双占据和空 σ 片断分子轨道(FMOs)组, $\phi_j \in \pi$ FMO组, $\phi_k \in$ 单占据 σ FMO组, 它们都精确地定域在各自的片断内; (2)利用 $\Phi^{\circ}l'$ 与 $\Phi^{\circ}l$ 间的重叠积分值($S'l' > 0.5$), 可以从DSI $^\circ$ 态中, 自动地选出Ns个对称的、由单占据轨道线性组合而成的分子轨道 $\Phi^{\circ}l' = \sum a_k l' \phi_k (k=1, 2, \dots, N_s)$, 接着, 用 $\Phi^{\circ}l'$ 取代FUL态中同类的、非对称轨道组 $\Phi_l = \sum a_k l \phi_k (k=1, 2, \dots, N_s)$; (3)以上述新的轨道组 $[\Phi^{\circ}l', \Phi_n, \Phi_m]$ 为基(其中 $\Phi^{\circ}l' \in$ DSI $^\circ$ 态, 它们离域于整个分子; 双占据及空 σ FMO组 Φ_m 和 π FMO组 Φ_n 属于FUL态), 按FUL态的条件, 再次对分子作有条件的RHF运算, 从中得到一组对称的、闭壳层正则FMOs, 而且每一个FMO均有正确的电子占据数; (4)利用Perkin原理, 将第3步所得的正则FMO组定域成一个对称的键轨道基组 $[\Phi_l', \Phi_n', \Phi_m']$ 。在这个基组中, π 体系 Φ_m' 与 σ 构架 Φ_n' 是彻底分离的, 而且这两个轨道组始终精确地定域在各自的片断内。

关键词 [蒾二烯](#) [微扰分子轨道法](#) [分子轨道计算](#) [定域化](#)

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A procedure for constructing a highly localized and symmetrical bond orbital basis set

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Abstract A procedure for constructing a highly localized and symmetrical bond orbital basis set with the π systems separated off from the σ frameworks has been developed. It is a four - step procedure: (1) over the opened - shell localized fragment molecular orbital (FMO) basis set $[\phi_k, \phi_i, \phi_j]$ where $\phi_i \in$ doubly occ. and vacant σ FMOs, $\phi_j \in \pi$ FMOs, and $\phi_k \in$ singly occ. FMOs, the conditional RHF computations provide each of the FUL and DSI $^\circ$ electronic states of a molecule, such as norbornadiene with a set of the closed - shell FMOs; (2) the symmetrical MOs, $\Phi^{\circ}l' = \sum a_k l' \phi_k (k=1, 2, \dots, N_s)$ which have delocalized over the whole molecule, in the DSI $^\circ$ substitutes for the unsymmetrical $\Phi_l = \sum a_k l \phi_k$ in FUL state, and those together with other two groups of the unsymmetrical FMOs, $\Phi_m = \sum a_j m \phi_j$ and $\Phi_n = \sum a_i n \phi_i$ in the FUL state formed a closed - shell FMO basis set $[\Phi_n, \Phi_m, \Phi^{\circ}l']$ in which each of FOMs Φ_n and Φ_m is still localized on its corresponding fragment; (3) based on the basis set $[\Phi_n, \Phi_m, \Phi^{\circ}l']$, the conditional RHF computation for molecule is performed under the following constraint: all $F_{ij} = 0.0$ and $S_{ij} = 0.0 (i \neq j, i \in \text{fragment } Q, \text{ and } P \neq Q)$ except for those between $\Phi^{\circ}l'$. It provides a molecule, such as norbornadiene, with a highly localized and symmetrical FMO basis set $[\Phi_n', \Phi_m', \Phi_l']$; (4) each of the FMOs Φ_n' , Φ_m' and Φ_l' is concentrated on a specific atom or two neighboring atoms using the Perkin procedure at last, and it has correct orbital occupancy.

Key words [PERTURBATION MOLECULAR ORBITAL](#) [MOLECULAR ORBITALS CALCULATIONS](#) [LOCALIZATION](#)

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