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Multi-Partitioning QDPT and Difference-Dedicated CI Calculations of Non-Adiabatic Couplings: Application to Charge Transfer in LiF System

Sergei Adamson (1,*), Andrei Zaitsevskii (1), Andrei Dement’ev (2) and Nicolai Stepanov (1)

(1) Laboratory of Molecular Structure and Quantum Mechanics, Chemical Department, M. Lomonosov Moscow State University, 119899 Moscow, Russia
(2) Inorganic Chemistry Department, Moscow State Pedagogical University, Nesvizhskii per., 119882 Moscow, Russia

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Abstract. — Potential energy and non-adiabatic coupling functions for the two lowest \( ^1\Sigma^+ \) states of LiF were calculated using the recently proposed perturbative approach, based on the multiple partitioning of the full Hamiltonian, and the difference-dedicated CI method. The results are compared with MRDCI and available full CI data for the same AO basis set. A high accuracy was achieved with a semiempirical perturbative scheme combining the direct calculations at second order with an approximate estimation of higher-order local contributions.

1. Introduction

Theoretical studies of the charge transfer reactions \( A + B = A^+ + B^- \) or \( A^+ + B = A + B^+ \) involving atoms or polyatomic systems require accurate estimations of several adiabatic potential energy surfaces and nonadiabatic couplings for the AB supersystem. \( \textit{Ab initio} \) methods commonly used in such computations are represented by different variants of the MCSCF, multireference CI (MRDCI) and perturbative CI techniques [1–7].

The MCSCF method is normally considered as a low-cost tool for qualitative description of potential energy surfaces and nonadiabatic couplings in a wide range of molecular geometries. Its complete-active-space (CAS) version is size-consistent, thus allowing one to study complex many-electron systems as well as simple molecules. However, this technique hardly provides quantitative results, since it is not well-suited for reproducing the dynamic correlation effects, which differ significantly for the electronic states with different charge distributions [1–3]. At present the MCSCF approach, usually with state-averaged energy functionals [8,9] is employed only to construct well-balanced MO basis sets for subsequent higher-level \( \textit{ab initio} \) calculations.

A considerable fraction of dynamical correlations can be taken into account by the MRDCI methods which have already proved to be a reliable tool for investigations of charge

(*) Author for correspondence (e-mail: adamson@moleq.chem.msu.su)

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transfer processes involving small molecules [1–3]. Unfortunately, the lack of size-consistency and computational cost rapidly increasing with the number of electrons can block their practical applications to complex polyatomic systems.

The perturbative CI techniques (i.e. generalisations of the CIPSI method and related procedures) [4–7] yield results close to MRDCI ones with a more reasonable computational cost. But as well as MRDCI these approaches are not size consistent. The size inconsistency problem is particularly serious for the effective interactions between the starting (variational) multi-configurational wave functions [10] which are critically important in the studies of avoided crossings [7]. It should be noted also that such methods impose certain undesirable constraints on the composition of the reference-space part of the wave functions after the variational step [10].

A promising alternative might consist in using the methods of the many-body quasi-degenerate perturbation theory (QDPT) which describe adequately the effects of dynamic correlation on the composition of wave functions and enable to achieve a strict size consistency [10]. While most of them suffer from numerical instabilities in the presence of intruder states, this difficulty is avoided in the recently proposed generalised Moller-Plesset quasi-degenerate perturbation theory based on the multiple partitioning of the total Hamiltonian (MPPT) [11]. Restricted at the second order, the state-selective version of MPPT combines numerical stability with exact size consistency and very low cost of computations. Another potentially useful approach implicitly based on the perturbation theory is the difference-dedicated configuration interaction technique (DDCI). Being rather economical, it provides highly reliable estimates of the energy differences in small molecules [12,13]. Though the DDCI method is not strictly size-consistent, it satisfies the "weak separability" condition [10]; this feature allows to apply this method to the description of local processes in large systems.

In spite of potential advantages of the above mentioned approaches, no studies of the performance of the MPPT scheme in non-adiabatic coupling calculations have been reported; as for the DDCI method, additional crude approximations (diabatic MO hypothesis and simple effective Hamiltonian model) has been used in such study [14].

In the present work we investigate the performance of MPPT and DDCI approaches as applied to the ionic-neutral avoided crossing and non-adiabatic coupling \( g_{12}(R) = \langle 1^1\Sigma^+ | \frac{\partial}{\partial R} | 2^1\Sigma^+ \rangle \) in the Li-F charge transfer system. An accurate description of electron correlations is known to be of crucial importance for reproducing its characteristics; for instance, an underestimation of dynamic correlations can displace the position of the avoided crossing region by several bohrs [1–3,13]. Moreover, the number of electrons which should be explicitly correlated is relatively large; this contrasts with the major part of previous studies which were restricted to systems with 2-4 electrons [4–7]. We employed fully numerical approach taking into account both orbital and CI contributions to the coupling coefficients as well as analytical formula. A new semiempirical computational scheme is formulated and tested. Our results are compared with those obtained by full CI and MRDCI methods [3].

2. Methods of Calculation

A detailed description of the second-order state-selective MPPT and DDCI schemes can be found elsewhere [11,12]. The reference (model) space was generated by the state-averaged CASSCF procedure [15]. The choice of two-dimensional active MO space as \((4\sigma,5\sigma)\) ensured a proper description of both neutral \((\text{Li}(2\text{S}) + \text{F}(3\text{P}))\) and ionic \((\text{Li}^+(4\text{S}) + \text{F}^-(1\text{S}))\) dissociation limits.
Since the calculation results should depend critically on the theoretical estimation of the electron affinity of F atom [2, 3], one cannot expect to achieve a high accuracy at the second order of MPPT. To improve the results we suggest a simple semiempirical scheme taking into account higher-order local contributions. This scheme implies the use of localized MO sets and incomplete (though separable) model spaces.

The sets of active spinorbitals, localized on the fragments A and B and the set of dissociation limits define several pairs of complete model spaces $\left( L^\mu_A, L^\nu_B \right)$ where $\mu, \nu$ indicate the states of free fragments A and B. We choose the model space $\left( L_{AB} \right)$ for the whole system as a sum of antisymmetrised direct products $L_{AB} = \bigoplus (L^\mu_A \otimes L^\nu_B)$. The space $L_{AB}$ is a subspace of the complete model space, associated with the total set of active spinorbitals. Then we introduce the diagonal shift of second-order effective Hamiltonian $H^{(2)}_{\text{eff}}$ to $H_{\text{eff}} = H^{(2)}_{\text{eff}} + \Lambda$ in the $L_{AB}$ space

$$\Lambda = \sum_{\mu\nu} P_{\mu\nu} \lambda_{\mu\nu},$$

where $P_{\mu\nu}$ projects onto the $(L^\mu_A \otimes L^\nu_B)$ subspace. The parameters $\{\lambda_{\mu\nu}\}$ are chosen in such a way that the diagonalization of $H_{\text{eff}}$ for infinite separation of fragments provides the correct relative positions of dissociation limits. These values are further used in the calculations of the A...B supersystem at finite separations; therefore the dependence of local higher-order contributions on the interaction of fragments is neglected. It should be stressed that the parameter adjustment requires only the information concerning free fragments A and B and their ions. In that follows we shall refer to this scheme as to MPPT/SE. In our example we have to consider two-dissociation limits, neutral ($\text{Li}^2(2S) + \text{F}(2P)$) and ionic ($\text{Li}^+(1S) + \text{F}^-(1S)$). At the dissociation, the localized active MO’s 4\sigma and 5\sigma correlate with the 2p\text{F} and 2s(\text{Li}) AO’s respectively and we have $L_{\text{LiF}} = L^{2S}_{\text{Li}} \otimes L^{2P}_{\text{F}} \oplus L^{1S}_{\text{Li}} \otimes L^{1S}_{\text{F}} = (\ldots 4\sigma 5\sigma) \oplus (\ldots 4\sigma 2\sigma)$, where spatial configuration symbols are used to denote subspaces associated with all possible spin factors.

For the sake of direct comparison of our results with the full CI ones [3] we used the same contracted Gaussian basis sets (9s4p)/[4s2p] for Li and (9s6p1d)/[4s3p1d] for F atoms which we shall denote as BL.

To obtain the localized MO’s satisfying the state-averaged MCSCF equations, we applied the projection technique [16] to the inactive, active and secondary subsets separately. The reference orbitals of free fragments were constructed by solving the atomic SCF equations for the fractional orbital occupancies [17] corresponding to the “intermediate” ($\text{Li}^+ + 0.5\text{F}^− - 0.5$) atomic charge distribution.

In order to avoid the problems associated with the non-orthogonality of eigenvectors, we employed the Hermitian form of effective Hamiltonians [18]. To ensure a proper comparison of the MPPT/SE scheme with other approaches, the choice of shift parameters $\{\lambda_{\mu\nu}\}$ in (1) corresponded to the estimations of ionization potential of Li and electron affinity of F within the same basis set. Note that the latter value and therefore the neutral-ionic energy difference at the dissociation limit differ significantly from experimental data (see Tab. 1).

A finite-difference scheme with the step of the differentiation equal to 0.001 a.u. has been used in the $g_{12}(R)$ calculations. The scheme was implemented by one of authors (S.A.). In all cases, the molecular centre of mass was placed at the origin of the coordinate system. In MPPT and MPPT/SE calculations of $g_{12}(R)$ matrix elements, the contributions from outer space projections of approximate wave functions were neglected. For MCSCF, DDCI and MRDCI multiconfigurational wave functions the $g_{12}(R)$ matrix elements were also calculated using the Sidis formula [19].
Table I. — *The ionic-neutral energy difference at the dissociation limit and characteristics of the avoided crossing point. Energy difference values are in eV, other values in atomic units.*

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta E_\infty$</th>
<th>$R_c$</th>
<th>$g_{12}(R_c)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSCF (a)</td>
<td>3.820</td>
<td>7.8</td>
<td>0.354</td>
</tr>
<tr>
<td>DDCI (a)</td>
<td>2.595</td>
<td>10.8</td>
<td>0.751</td>
</tr>
<tr>
<td>MRDCI (a)</td>
<td>2.508</td>
<td>11.1</td>
<td>0.808</td>
</tr>
<tr>
<td>MPPT (a)</td>
<td>3.042</td>
<td>9.5</td>
<td>0.466</td>
</tr>
<tr>
<td>MPPT/SE (a)</td>
<td>2.456</td>
<td>11.2</td>
<td>0.796</td>
</tr>
<tr>
<td>FCI (b)</td>
<td>-</td>
<td>11.4</td>
<td>-</td>
</tr>
<tr>
<td>MPPT/SE (c)</td>
<td>1.992</td>
<td>13.7</td>
<td>1.980</td>
</tr>
</tbody>
</table>

(a) BL basis set.
(b) Reference [3].
(c) Calculations with EXT basis set and the shift value derived from experimental atomic data.

3. Results and Discussion

The adiabatic potential curves along with corresponding $g_{12}(R)$ functions obtained by the finite-difference technique are presented in Figure 1. Since the full CI non-adiabatic couplings are unavailable, we have to compare the corresponding results with those from the MRDCI calculations which are expected to be only slightly poorer than the full CI data [3].

The numerical results are summarized in Table I. The position of avoided crossing ($R_c$) is accepted to coincide with that of the maximum of $|g_{12}(R)|$. The neglect of dynamic correlation effects at the MCSCF level resulted in a strong underestimation of $R_c$ and $g_{12}(R)$ values. The incorporation of these correlations at the second order in MPPT lead to certain improvements which were far from being radical. An insufficient accuracy of the second-order results should be attributed to a slow convergence of electron affinity estimates for F. The inclusion of approximate higher-order local corrections brought the results in a perfect agreement with the MRDCI and full CI data. A reasonable accuracy was also achieved with the DDCI method; the difference in dynamic correlation effects between the ionic and neutral structures and therefore $R_c$ were slightly underestimated.

A good agreement of the avoided crossing parameters from the MPPT/SE calculations with MRDCI and full CI data induced an attempt to perform the computations with a more reliable basis set, shifting the ionic-neutral energy difference at the dissociation to the experimental value of 1.992 eV [4]. The extended AO basis set (EXT) was obtained from the standard (10s6p)/[5s3p] sets for Li and F [20] by adding s and p diffuse functions (exponential parameters $\alpha_s = \alpha_p = 0.0074$) and polarization d functions centred on Li ($\alpha_d = 0.2$); the F basis set was augmented with the s and p functions ($\alpha_s = \alpha_p = 0.1076$) and three sets of d functions ($\alpha_d = 2.8, 0.7, 0.2$).

The adiabatic potential energy curves and the $g_{12}(R)$ function, obtained by MPPT with semiempirical correction are displayed at Figure 2; the $R_c$ value is estimated as 13.7 a.u. diabatic curves, constructed from the initial adiabatic curves by numerical integration are presented at the same figure. It is of interest to note that one of the diabatic potential curves is practically identical with the ionic Rittner’s potential curve [21],

$$E(R) = \Delta E_\infty - \frac{1}{R} - \frac{(\alpha(Li^+) + \alpha(F^-))}{2R^4}$$

constructed using the experimental value of the energy difference at the dissociation ($\Delta E_\infty$).
and the polarizabilities $\alpha$ of the Li and F ions 0.193 a.u. and 15.54 a.u. respectively [3].

The calculation with the Sidis formula yielded the $R_c$ values close to those given by the finite-difference scheme at the same level of approximation. However, $g_{12}(R)$ values were overestimated by 3–3.5 times. This result clearly indicates that the use of Sidis formula in nonadiabatic coupling calculations requires to employ the approximate multi-configurational wave functions of much better quality than those employed in our work.

It should be noted that the ionic dissociation limit $(F^- (1S) + Li^+ (1S))$ lies slightly above the second neutral limit $(F (2P) + Li (2P))$ (1.848 eV). Therefore one more low-lying ionic-neutral avoided crossing $(2^1\Sigma^+ - 3^1\Sigma^+)$ can be found for the LiF system. To extend our study to this peculiarity, we had to add the $6\sigma$ MO correlated with the $2p_2$ AO Li to the active manifold. According to the MPPT/SE estimations, the region of strong non-adiabatic interactions $2^1\Sigma^+ - 3^1\Sigma^+$ was localized at the very large internuclear separations (ca. 190 a.u.) and clearly cannot be related to any physical charge transfer process.
4. Conclusions

The MPPT and DDCI methods with MCSCF reference space were applied to describe the non-adiabatic couplings of LiF in the region of the neutral-ionic avoided crossing. The starting state-average MCSCF approximation failed to describe adequately the coupling as well as the peculiarities of the potential curves because of the neglect of dynamic correlation effects. The second-order MPPT combined with a semiempirical incorporation of local higher-order effects brings the results into quantitative agreement with those from much more expensive MRDCI and full CI calculations. Being strictly size-consistent and extremely economical, this approach appears to be potentially powerful tool for studies of charge-transfer reactions in much larger systems. Rather accurate results were also obtained with the DDCI method. Moreover, recent studies allow to hope that further improvement is possible via iterative construction of difference-dedicated pseudonatural orbitals [13,14]. The use of Sidis analytical formula for non-adiabatic couplings in quantitative calculations requires to employ much better approximations.
for the wave functions than those considered in our work. Being efficient for the molecules with 2 valence electrons [4], it seems to be useless for the systems with larger number of electrons.

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