For surfaces not containing a basin at the equidistant linear configuration, a steepest-descent method is more appropriate for determining the least-energy trajectory. Starting at the saddle point, the path is traced out by advancing in short increments, here taken to be 0.01 bohr, in the direction of steepest descent. The paths obtained in this manner for the Porter–Karplus,[1] Sato[8] ($k=0.18$), and London[6,11] potential surfaces are shown in Fig. 1.

The absence of kinks along the four semi-empirical reaction paths given in Fig. 1 serves to lend credence to the use of such potential surfaces to represent the H_3 system. In particular, one need not harbor reservations with regard to these potentials on account of their curvature near the transition point. Furthermore, other surfaces,[12–15] derived from similar principles and applied to other reaction systems, should also be well behaved in this respect.

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Comments

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Medium Rearrangement Energy in the Theory of the Solvated Electron

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Tachiya[1] has re-evaluated the medium polarization energy in the theory of localized excess electron states in polar liquids. His analysis is valid within the framework of the continuum model which considers[2] the trapping centre as a cavity in a continuum dielectric medium. This interaction term is crucial[2] for the evaluation of the heat of solution of the excess electron within the framework of the continuum model. In my original work[2] the medium polarization energy has been underestimated, as the contribution of the fraction of the electronic charge enclosed in the cavity was not included in the estimate of the orientational polarization energy. This sin of omission was amended in more recent work,[3,4] while Land and O'Reilly[5] have derived a more refined dielectric SCF version for this interaction term.[6] It should be noted that (unlike stated by Tuchiya[1]) since in early theoretical work[2] the medium polarization energy did include just the orientational polarization term, while the electronic polarization was incorporated in the electronic energy.

I would like to take this opportunity to comment on the general problem of the medium rearrangement energy, E_r. The total equilibrium ground state energy, E_t, of the excess electron in a polar solvent is given in terms of the electronic energy, E_e, in the form $E_t=E_e+E_r$, and in general $E_r\geq 0$ and $0\geq E_t\geq E_e$. It is now realized[5,7,8] that pushing the continuum model[2] down to the cavity boundary involves a gross oversimplification of the short range electron-medium interactions. A more refined approach to this problem involves an electrostatic molecular model,[5,7] where an electrostatic microscopic potential field is applied to account for short range electron solvent interactions due to the oriented solvent dipoles in the first coordination layer, while the Landau[9] continuum dielectric potential[2] (corrected[7] for "background" energy via the Wigner Seitz model[10]) was retained to account for long range attractive interactions beyond the first solvation layer. Within the framework of this model, the medium rearrangement energy is[7] $E_r=E_{ST}+E_{pV}+E_{dd}+E_{HH}+\Pi$, where E_{ST} is the (small) surface tension term accounting for the formation energy of a void, E_{pV} is the pressure-volume work, E_{dd} is the electrostatic repulsion energy of the oriented dipoles in the first coordination layer, E_{HH} is the contribution of short range intermolecular repulsions in the first coordination layer, and finally Π corresponds to the long range medium orientational polarization energy outside the first solvation layer. The latter term was handled[7] by the Land–O'Reilly equation.[5] Thus the medium orientational polarization energy just provides one component to the total medium rearrangement energy. The theory of excess electron states in polar fluids cannot be quantitatively and rigorously handled by the continuum model. The molecular model[5,7] provides a first step towards a better theoretical understanding of the solvated electron, in particular its ground state configurational stability and its optical properties.

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Errata

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Erratum: Molecular Scattering Factors for H_2, N_2, LiH, and HF

[J. Chem. Phys. **56**, 280 (1972)]

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The statement that the $a_J(\kappa)$ coefficients, $J>0$ are identically zero for F^- in the IA approximation is incorrect (p. 284, line 1; p. 286, line 40). This equality would be true if the molecular center lay at the fluorine nucleus, but our center lies at the midpoint of the HF axis. The correct F^-IA coefficients differ from the corresponding MO coefficients in Table II by less than 3% for $a_0(\kappa)$ and 5% for $a_1(\kappa)$ and $a_2(\kappa)$ up to $\kappa=5.5$ Å^{-1}. Gas scattering differences run at about 2%.

The conclusion that molecules composed of first row atoms do not have enough inner electrons to allow one to ignore bonding distortions in scattering factor calculations remains unchanged. If distortions were negligible, the H^0, F^0, and LiH IA calculations would have agreed more closely with their respective MO counterparts.

Other errata are: p. 283, line 51: change "a_0 coefficient" to "gas scattering." Figures 3 and 4: multiply ordinate scale values by 0.1.