

Molecular structure of one-electron diatomic molecules subject to plasma screening and its effect on the dynamics.

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Synopsis The effect of plasma screening on the electronic and vibrational structure of one-electron diatomic molecules is analyzed by including screened Coulomb interactions among all their particles in the solution of the Schrödinger equation. The breakdown of the well-known separability of the Schrödinger equation in confocal elliptical coordinates, the loss of long-range Coulomb interaction and the non-degeneracy in both the united atom and separated atom limits bring new elements into the analysis of the modified binding energies (electronic and vibrational), adiabatic correlation rules, molecular Stark mixings due to polarization effects, unexpected presence of molecular shape resonances and changes in non-adiabatic and radiative couplings upon the variation of the screening strength.

The introduction of screening in the Coulomb interaction between charged particles appears in many fields of plasma, atomic, molecular and solid state physics. Screening effects may strongly modify the electronic and vibrational structure of molecules and their related properties and interactions. We analyze screening effects in the most simple one-electron molecules, H_2^+ and HeH^{2+} . The two-center (Z_1, e^-, Z_2) unscreened Coulomb problem is well known to be separable and exactly solved in confocal elliptical coordinates so that the electronic wavefunction can be written as the product $\Psi^m(\mathbf{r}; R) = \Lambda_{km}(\xi) M_{qm}(\eta) \Phi_m(\phi)$. The preservation of the number of nodes (k, q, m) from the united atom (UA) limit to the separated atom (SA) one fully determines the UA-SA correlation rules. In contrast, when screening is introduced this separability is lost and one is bound to solve the Schrödinger equation (even in the UA or SA limits), by diagonalizing the Hamiltonian that contains the screened potential $V(r_1, r_2, R) = -Z_1 e^{-\lambda r_1}/r_1 - Z_2 e^{-\lambda r_2}/r_2 + Z_1 Z_2 e^{-\lambda R}/R$. We use an expansion in the form $\Psi^m(\mathbf{r}; R) = \sum_{i\ell} c_{i\ell}^m (\xi^2 - 1)^{|m|/2} B_i(\xi) \Theta_\ell^m(\eta) e^{im\phi}$, in terms of B-splines $B_i(x)$ and associated Legendre polynomials $\Theta_\ell^m(x)$ and obtain very accurate energies and wavefunctions to construct the new distorted adiabatic correlation diagrams ($E_n[R]$ vs. R) for any arbitrary value of λ . The change against λ of the binding energy at the new equilibrium distances (R_e , $E_n[R_e]$) for those states that display a minimum ($1s\sigma_g$, $2p\pi_u$, $3d\sigma_g$, $4f\sigma_u$, etc) produces a varying number of supported vibrational states. For large enough λ , many molecular states of the Rydberg series become

unbound. Real crossings among states in the unscreened case become now avoided ones in the presence of screening with an interchange of character that depends on the screening strength. In contrast to the unscreened case, where states do dissociate in the SA limit as Stark hybrids, the screened diatomic molecule dissociates into spherical atoms. However, very diffuse non adiabatic radial couplings among states dissociating to the same non-degenerate atomic shell in the SA limit show Stark mixing as R decreases due to polarization effects. Both radial and radiative dipolar couplings are computed and compared for $\lambda \in [0, 1.5]$ (including the unscreened exact case $\lambda=0$) to show that some couplings vanish at $R \rightarrow \infty$ when $\lambda > 0$. These effects indicate that screened one-electron molecules partially share properties pertaining more to the case of unscreened many-electron diatomic molecules dissociating into neutrals than to the unscreened one-electron molecule. Also, it is known that in the UA limit, the screened hydrogenic atoms like He^+ show a series of shape resonances in the continuum for $\ell > 0$ [1]. We show that these atomic shape resonances *survive* in the screened molecular case as $R > 0$. In addition, the screening conditions under which Borromean states appear are analyzed. All this structure analysis is required prior to perform any simulation for ion-atom collisions [2] or molecular photodynamics while under the influence of a Debye plasma.

References

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