Curve Crossings and Constraints in Molecular-Orbital Correlations

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The unexpected crossing of molecular-orbital energy curves recently observed by Fortner *et al.* for slightly asymmetric multiply charged collision systems is explained in the framework of a Hartree-Fock theory with a constraint enforcing unequal charge sharing between the subsystems.

The excitation of inner-shell electrons in low-velocity ion-atom collisions has been an area of extensive investigation. One of the best evidences for the quasimolecular excitation mechanism proposed by Fano and Lichten[1] is the dependence of K-vacancy production[2] on the presence of $2p$ vacancies in the high-Z collision partner prior to the collision. During the in-going part of the collision these vacancies move along the $2p\pi$ molecular level until, close to the united-atom (UA) limit, they may be transferred by rotational coupling to the $2p\sigma$ level which in turn correlates to the separated-atom (SA) $1s$ level of the low-Z partner. In order to determine whether a given UA level adiabaticallycorrelates to the high-Z or low-Z partner it is customary to invoke the von Neumann–Wigner noncrossing rule.[3] The rule states[4] that adiabatic MO energy curves with like symmetries should not cross.

In recent experiments Fortner *et al.*[5] have investigated ion-atom collisions with multiply charged projectiles ($Ne^{n+}+CH_4, N_2, O_2$, Ne and $N^{n+}+CH_4, N_2, O_2$) in the energy range of 50–500 keV. The experiments include collision systems in which, because of unequal charge sharing, the low-Z partner has a lower $2p$ energy than the high-Z partner. In the following, we denote this as unnatural ordering of the SA levels. The experimental data show that MO correlation diagrams for ionized quasimolecules obtained[6] from an effective single-electron Hamiltonian (required to give the correct SA level sequence) do not produce the correct correlations. Rather the system behaves as if none of the partners were ionized. In other words, the $2p\pi$ MO correlates to the SA $2p$ state of the high-Z partner irrespective of the incident charge state of the projectile, that is, irrespective of the level sequence in the SA limit. This remarkable fact indicates that for unnatural-ordering levels with like symmetries do cross and thus appear to violate the noncrossing rule. In the following, I show that this rule does not apply. The levels are neither adiabatic nor diabatic[2] in the usual sense.

When invoking the noncrossing rule one has, of course, to keep in mind that the picture of independent MO's is a simplification. The actual system has more degrees of freedom and hence a larger number of symmetries (known or unknown) than an effective single-electron system.[3] In fact, charge sharing is a degree of freedom characteristic for a many-electron system. Since the MO picture is quite appropriate[2] in most situations we have to examine the effect of additional degrees of freedom on the noncrossing rule for single-particle energy curves.

The natural way to construct molecular orbitals from the actual many-electron problem is furnished by the Hartree-Fock (HF) procedure. The method leads[7] to the single-particle equations

$$F\varphi_i = \epsilon_i \varphi_i, \tag{1}$$

which have to be solved self-consistently. Here, F is the Hartree-Fock operator

$$F = h + v^{\mathrm{HF}},$$

with

$$h = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2 Z_1}{|\vec{r} - \frac{1}{2}\vec{R}|} - \frac{e^2 Z_2}{|\vec{r} + \frac{1}{2}\vec{R}|}, \tag{2}$$

where the midpoint between the nuclei (situated on the z axis at a distance R from each other) has been chosen as the orign. Here v^{HF} is the HF potential. For a neutral quasimolecular system the method leads to individually neutral separated atoms with the adiabatic correlations governed by the noncrossing rule.

For multiply ionized systems the quasimolecular ground state is obtained by sharing the total charge $k = k_1 + k_2$ (where the individual charge states are $k_{1,2} = Z_{1,2} - N_{1,2}$) for large R are nearly equally as possible between the separating partners.[8,9] In collision studies, however, one often deals with markedly unequal charge sharing in the entrance channel. This corresponds to an

excited state from the point of view of the adiabatically relaxed quasimolecule and in certain cases[5] is associated with an unnatural level sequence. We have previously[10] discussed this problem in the framework of perturbation theory.

In this note I want to present a simple argument which should also be applicable to other physical systems. The problem is to construct single-electron states for quasimolecular systems with asymptotically unequal charge sharing[9] (e.g., the system $N^{++}+O$ or $N^{++}+Ne$). This can be done by imposing a constraint on the system: In a complete time-dependent description the system would evolve from an experimentally prepared initial charge sharing k_1, k_2 (for definiteness assuming $k_1+k_2=$ even) through an intermediate stage where the partners mutually polarize each other unequally (since $k_1 \neq k_2$) to the UA system where the electrons cannot be assigned to any one of the partners. Presently we cannot carry out such a treatment. In order to simulate some features of this time evolution in the in-going part of the collision we require the total electronic dipole moment to be $(N_1-N_2)R/2$ for large R and to decrease faster than R with smaller separations. Expressing this dynamically caused charge equilibration by a connection function $f(R)$ which decreases from 1 at $R=\infty$ to 0 at $R=0$, I prescribe

$$\langle \textstyle\sum_\mu \tilde{z}_\mu \rangle = f(R)(k_2-k_1) \tag{3}$$

with

$$\tilde{z}_\mu = \frac{z_\mu}{\frac{1}{2}R} - \frac{Z_1-Z_2}{N_1+N_2}. \tag{4}$$

Here, the angular brackets denote the ground-state expectation value and z_μ is the z coordinate of the μth electron. The function $f(R)$ makes sure that with $R \to 0$ the subsidiary condition (3) loses its significance and the constrained solution merges smoothly into the unconstrained solution. The detailed form is of no importance for the present argument (it is relevant for the position, not for the existence, of curve crossings). The variational problem with the constraint (3) is formulated with the aid of a Lagrange multiplier λ as

$$\delta\langle H - E' - \lambda \textstyle\sum_\mu \tilde{z}_\mu \rangle = 0. \tag{5}$$

Clearly, λ has the physical significance of an external electric field in the z direction. Noting that $\tilde{z}_\mu$ is a single-particle operator one derives the constrained HF equations

$$F' \varphi_i' = \epsilon_i' \varphi_i' \tag{6}$$

with

$$F' = F - \lambda \tilde{z}, \tag{7}$$

where the potential v^{HF} in Eq. (2) is evaluated with the functions φ_i'. The effective single-particle equation (6) has to be solved self-consistently subject to the condition (3) which allows one to determine λ. We may now define "constrained physical MO energies" by the expectation values (not eigenvalues)

$$e_i = \langle \varphi_i' | F | \varphi_i' \rangle = \epsilon_i' + \lambda \langle \varphi_i' | \tilde{z} | \varphi_i' \rangle. \tag{8}$$

There are defined in contrast to the "eigenenergies of the constrained problem," ϵ_i', and the "adiabatic MO energies of the unconstrained problem," ϵ_i. The definition (8) of the "constrained physical" MO energies implies their identification with single-electron energies.

Let us now turn to the noncrossing rule. The rule is expected to apply to the eigenvalues $\epsilon_i'(R)$ of the single-particle problem (6). The usual proof[3,4] can be carried over literally to Eq. (6). It then follows immediately from Eq. (8) that the "constrained physical" MO energy curves e_i may freely cross each other provided the energy shifts $\lambda\langle \tilde{z} \rangle_i = \lambda \langle \varphi_i' | \tilde{z} | \varphi_i' \rangle$ (which have opposite signs for the two partners) are large enough to reverse asymptotically the order of the energies e_i as compared to the ϵ_i' (cf. Fig. 1). This is the case if the level shifts are both greater than one-half the asymptotic energy difference $\Delta e = |e(H) - e(L)|$. The magnitude of λ would result from a complete calculation but it can also be expressed[11] by the shift δE of the total energy of the constrained ground state with respect to the unconstrained ground-state energy (defined in the ϵ representation) through the relation

$$\delta E = \tfrac{1}{2}\lambda \textstyle\sum \langle \tilde{z} \rangle_i, \tag{9}$$

which is valid[11] if the Slater determinants for the ground states of the constrained and of the unconstrained problem are not orthogonal (i.e., for not too large R). The required reversal of level sequence occurs if

$$\left| \frac{\lambda \langle \tilde{z} \rangle}{\delta E} \right| = \left| \frac{2\langle \tilde{z} \rangle}{\sum \langle \tilde{z} \rangle_i} \right| > \frac{\Delta e}{2\delta E}. \tag{10}$$

Here, the right-hand side is asymptotically known (using $2p$ and total energies from Ref. 8 one obtains the values 1.13 for $N^{++}+O$, $N^{+}+O^{+}$, and 1.32 for $N^{++}+Ne$, $N^{+}+Ne^{+}$). The ratio will not change very much for decreasing R until one enters the region of strong level promotion. For compari-

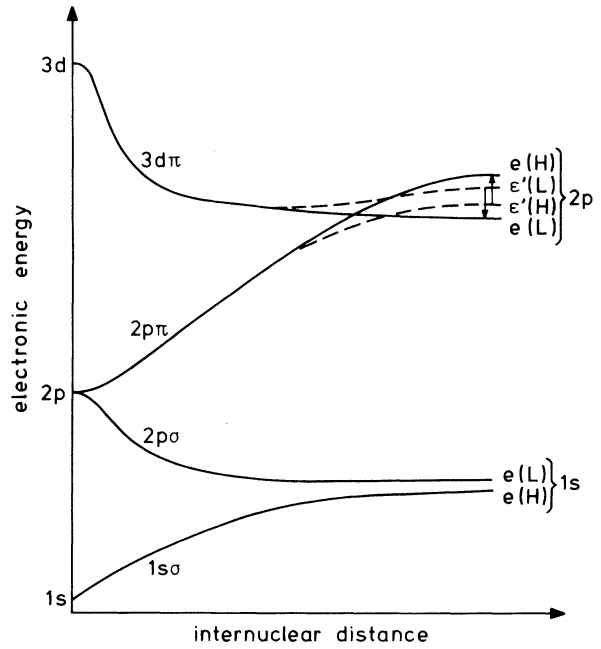

FIG. 1. Schematic correlation diagram for a slightly asymmetric collision system. The low-Z partner has a higher charge state than the high-Z partner, so that the order of the separated-atom $2p$ energies e is reversed [i.e., $e(L) < e(H)$] with respect to the natural level sequence. While the constrained eigenenergies ϵ' (see text) obey the noncrossing rule the "constrained physical" MO energies e do not. The unconstrained adiabatic energies ϵ are not shown. They behave similarly to the ϵ' with $\epsilon(H) < \epsilon(L)$. Also not shown are the ϵ and ϵ' levels for the SA $1s$ states.

son, one has asymptotically $|\langle\tilde{z}\rangle_i| = 1$ and $|\sum\langle\tilde{z}\rangle_i| = |k_1 - k_2|$. However, for finite separations R where Eq. (9) is valid $|\sum\langle\tilde{z}\rangle_i|$ will be considerably reduced because of the unequal mutual polarization of the constituents of the quasimolecule. We then expect the inequality (10) to hold (at least in suitable cases), so that the order of the "constrained physical" levels $e(H)$, $e(L)$ is indeed reversed with respect to the eigenenergies of the constrained problem $\epsilon'(H)$, $\epsilon'(L)$ (cf. Fig. 1) which obey the noncrossing rule in the same way as the adiabatic MO energy curves $\epsilon(H)$, $\epsilon(L)$ of the unconstrained problem. Since for each level i the curves ϵ_i', e_i, ϵ_i merge together for $R \to 0$, there will be level crossings for the "constrained physical" e_i curves. However, no violation of the noncrossing rule as it is usually applied to adiabatic levels is implied.

It seems that this mechanism for curve crossing has not been considered so far. If it is real there should be no charge-state dependence of physical correlations. The experimental data[5] not only suggest the existence of this effect but also show that the intersecting e_i curves do not appear to interact appreciably. The latter result is readily understood by noting that the radial coupling matrix elements

$$\langle\varphi_i'|(\partial/\partial R)|\varphi_j'\rangle = \langle\varphi_i'|(\partial v^{\mathrm{eff}}/\partial R)|\varphi_j'\rangle/(\epsilon_j' - \epsilon_i')$$

are governed by the energy differences between nonintersecting ϵ_i' curves and *not* by the "constrained physical" energies e_i. Of course, for a given collision system diabatic crossings may also occur. Their presence should manifest itself in the velocity dependence of the excitation cross section and in a certain sensitivity to the charge-state sharing which affects the distance of closest approach between adiabatic energy curves. More experimental information is needed on these points, in particular with still higher charge states. If the proposed mechanism exists it should be of great importance for collisions with highly stripped projectiles. Existing MO correlation diagrams for ionized systems derived from the HF approach[12] or an effective single-electron potential[6] may be inconclusive for the incident channel if the charge states of target and projectile are too different.

In conclusion it should be noted that the presently suggested approach to simulate some features of a complex time-dependent system by a constrained variational problem for single-particle states does not rely on details of the system considered and thus may be applicable to other physical situations as well.

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[9]If for k = odd or if as a result of shell effects the molecular ground state has unequal charge sharing, we take this as the reference state and re-interpret "unequal charge sharing" as a deviation from this charge sharing.

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Spontaneous Emission near the Electron Plasma Frequency in a Plasma with a Runaway Electron Tail

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Spontaneous emission of radiation with frequencies near the electron plasma frequency is studied for a plasma which consists of both thermal and runaway electrons. It is found that a substantial enhancement of the spontaneous radiation intensity can occur in this frequency regime via a Cherenkov resonance with the runaway electrons. Numerical analysis indicates that, for reasonable estimates of densities and energies, the plasma-frequency radiation can attain levels greater than the peak thermal emission at the second gyroharmonic.

A great deal of interest has recently been focused on the question of high-frequency radiation from tokamak plasmas. In particular, recent observations have detected intense radiation at frequencies in the vicinity of the central electron plasma frequency of the device.[1-6] Since these emissions are correlated with the presence of high-energy runaway electrons, it has been proposed that the observed radiation is due to induced processes arising from the highly anisotropic nature of the runaway-electron distribution function.[7-9] In this work, however, we suggest that the emissions near the plasma frequency can be explained by a spontaneous-emission process. Specifically, the high energies characteristic of the runaway electrons permit the spontaneous emission of synchrotron radiation via a relativistic Cherenkov resonance. Numerical analyses, based upon reasonable estimates of tokamak operating parameters, indicate that the radiation levels in the vicinity of the plasma frequency can be comparable to the intensity of the emission at the peak in the thermal spectrum near the second gyroharmonic, which is in agreement with experiment.

The physical configuration we consider is that of a magnetized plasma which, in addition to a thermal background, contains a small population of suprathermal runaway electrons. We assume that the scale lengths for variation of the ambient magnetic field $\vec{B}_0$ ($\equiv B_0\hat{e}_z$) and electron density are much greater than the wavelengths of interest. Furthermore, it is assumed that the thermal energy of the background electrons is of the order of 1 keV, while the runaway energies may be, typically, several hundred keV. As a result, relativistic effects may be generally neglected in the computation of the thermal emissivity, but they must be retained in all phases of the computation of the runaway emissivity.

It is known that under the combined influence of an external electric field and Coulomb scattering, the runaway-electron distribution function is generally expected to possess a long flat tail in the

