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Bound and resonance states of the dipole-bound anion of hydrogen cyanide: competition between threshold effects and rotation in an open quantum system

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Bound and resonance states of the dipole-bound anion of hydrogen cyanide HCN⁻ are studied using a non-adiabatic pseudopotential method and the Berggren expansion technique involving bound states, decaying resonant states, and non-resonant scattering continuum. We devise an algorithm to identify the resonant states in the complex energy plane. To characterize spatial distributions of electronic wave functions, we introduce the body-fixed density and use it to assign families of resonant states into collective rotational bands. We find that the non-adiabatic coupling of electronic motion to molecular rotation results in a transition from the strong-coupling to weak-coupling regime. In the strong coupling limit, the electron moving in a subthreshold, spatially extended halo state follows the rotational motion of the molecule. Above the ionization threshold, electron’s motion in a resonance state becomes largely decoupled from molecular rotation. Widths of resonance-band members depend primarily on the electron orbital angular momentum.

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I. INTRODUCTION

Dipolar anions are one of the most spectacular examples of marginally bound quantum systems [1–11]. Wave functions of electrons coupled to neutral dipole molecules [12, 13] are extremely extended; they form the extreme quantum halo states [14–19]. Resonance energies of dipolar anions, including those associated with rotational threshold states, can be determined in high resolution electron photodetachment experiments [20–25]. Theoretically, however, the literature on the unbound part of the spectrum of dipole potentials, and multipolar anions in particular, is fairly limited [26–34].

The breakdown of the adiabatic approximation in dipolar molecules possessing a supercritical moment [35–39] caused by coupling of electron’s motion to the rotational motion of the molecule, is expected to profoundly impact the properties of rotational bands in such systems [25, 30, 31, 36], such as the number of rotationally excited bound anion states.

In this study, we address the nature of the unbound part of the spectrum of dipolar anions. In particular, we are interested in elucidating the transition from the rotational motion of weakly-bound subthreshold states to the rotational-like behavior exhibited by unbound resonances. The competition between continuum effects, collective rotation, and non-adiabatic aspects of the problem makes the description of threshold states in dipole-bound molecules both interesting and challenging.

Our theoretical framework is based on the Berggren expansion method (BEM) – a complex-energy resonant state expansion [40–42] based on a completeness relation introduced by Berggren [43] that involves bound, decaying, and scattering states. In the context of coupled-channel method, BEM was successfully applied to molecules [39] and nuclei [44–49]. The advantage of this method, which is of particular importance to the problem of dipole-bound anions when the rotational motion of the molecule is considered [39, 50], is that the BEM is largely independent of the precise implementation of boundary conditions at infinity.

This is not the case for other techniques such as, for instance, the direct method of integrating coupled-channel equations. Notable exceptions are basis-expansion methods relying on complex scaling [51–57]. By rotating radial coordinates in the complex plane by an given angle $\theta$, $r \to r e^{i\theta}$, the initial Hermitian Hamiltonian is transformed into a non-Hermitian one, whose bound eigenstates correspond to bound and resonant states of the system, the latter bearing complex energies. As complex-scaled wave functions all vanish for $r \to +\infty$, their asymptotic behavior does not have to be imposed explicitly and they can be obtained through a diagonalization of the rotated Hamiltonian in a set of square-integrable states [55, 57–60]. In particular, BEM has been benchmarked against complex rotation when both methods apply [59, 60]. However, rotation by an angle $\theta$ of the Hamiltonian is possible only if the potential is dilatation-analytic [61, 62]. This is obviously the case for the exact molecular Hamiltonian, but not necessarily the case.
for effective pseudo-potentials. In fact, pseudo-potentials can be non-analytical or diverge in the complex plane for small values of $\theta$, as is the case for the pseudo-potential studied in this paper. Complex rotation of the Hamiltonian is thus precluded. The BEM, on the other hand, can be conveniently applied. An alternative treatment, similar in spirit, is the complex eigenvalue Schrödinger equation (CESE) method [63, 64].

The calculations have been carried out for the rotational spectrum of dipole-bound anions of hydrogen cyanide HCN$^-$, which has long served as a prototype of a dipole-bound anion [4, 65] and was a subject of experimental and theoretical studies [25, 66, 67]. Here, we extend our previous studies [39] of bound states of dipolar molecules to the unbound part of the spectrum. To integrate coupled channel equations, we use the Berggren expansion method as it offers superior accuracy as compared to the direct integration approach for weakly-bound states and, contrary to direct integration approach, allows to describe unbound resonant states. Moreover, the knowledge of the asymptotic form of eigenfunctions is not necessary in our approach.

This paper is organized as follows. The model Hamiltonian is discussed in Sec. II. The coupled channel formulation of the Schrödinger equation for dipole-bound anions is outlined in Sec. III. The Berggren expansion method is introduced in Sec. IV. The parameters of our calculation are given in Sec. V. Section VI presents the technique adopted to identify the decaying Gamow states (resonances). To visualize valence electron distributions, in Sec. VII we introduce the intrinsic one-body density. The predictions for bound states and resonances of HCN$^-$ are collected in Sec. VIII. Finally, Sec. IX contains the conclusions and outlook.

II. HAMILTONIAN

The dipolar anions are composed of a neutral polar molecule with a dipole moment $\mu$ that is large enough to bind an additional electron. Since energy of the valence electron in an anion is very small as compared to energies of well-bound HCN electrons, this scale separation justifies the use an effective potential treatment of the halo [68–70]. In the present study, the HCN$^-$ dipolar anion is described in the Born-Oppenheimer approximation, and the intrinsic spin of an external electron is neglected [35], largely simplifying the equations [36]. Within the pseudo-potential method, the Hamiltonian of a dipolar anion can be written as:

$$H = \frac{p_e^2}{2m_e} + \frac{j^2}{2I} + V$$

where $I$ is the moment of inertia of the molecule, $p_e$ is the linear momentum of the valence electron, and $m_e$ its mass. The electron-molecule interaction $V$ is approximated by a one-body pseudo-potential [35, 71, 72]:

$$V(r, \theta) = V_{\text{dip}}(r, \theta) + V_0(r, \theta) + V_{Q_{zz}}(r, \theta) + V_{\text{SR}}(r),$$

where $\theta$ is the angle between the dipolar charge separation $s$ and electron coordinate;

$$V_{\text{dip}}(r, \theta) = -\mu e \sum_{\lambda=1,3,...} (r_{\lambda}/r)^{\lambda} \frac{1}{s_{\lambda}} P_{\lambda}(\cos \theta)$$

is the electric dipole potential of the molecule;

$$V_0(r, \theta) = -\frac{e^2}{4r^4} [\alpha_0 + \alpha_2 P_2(\cos \theta)] f(r)$$

is the induced dipole potential, where $\alpha_0$ and $\alpha_2$ are the spherical and quadrupole polarizabilities of the linear molecule;

$$V_{Q_{zz}}(r, \theta) = -\frac{e}{r^3} Q_{zz} P_2(\cos \theta) f(r)$$

is the potential due to the permanent quadrupole moment of the molecule, and

$$V_{\text{SR}}(r) = V_0 \exp \left[-(r/r_c)^6\right],$$

is the short-range potential, where $r_c$ is a radius range. The short-range potential accounts for the exchange effects and compensates for spurious effects induced by the regularization function

$$f(r) = 1 - \exp \left[-(r/r_0)^6\right]$$

introduced in Eqs. (4,5) to avoid a singularity at $r \to 0$. The parameter $r_0$ in Eq. (7) defines an effective short range for the regularization.

The dipolar potential $V_{\text{dip}}(r, \theta)$ is discontinuous at $r = s$. To remove this discontinuity, in Eq. (3) we replace

$$\begin{align*}
\frac{r_0}{r} &\to \left\{ \frac{r}{r_0} f_a(r) + \frac{x}{2} [1 - f_a(r)] \right\} \text{erf}(ar) \\
\frac{r}{r} &\to s f_a(r) + r [1 - f_a(r)]
\end{align*}$$

with $f_a(r) = (1 + \exp((r-s)/a))^{-1}$.

III. COUPLED-CHANNEL EQUATIONS

In the description of dipolar anions with the Hamiltonian (1), the coupled-channel formalism is well adapted to express the wave function of the system [1, 35, 72–74]. The eigenfunction of $H$ corresponding to the total angular momentum $J$ can be written as

$$\Psi^J = \sum_{c} u_{cJ}(r) \Theta_{cJ}(r),$$

where the index $c$ labels the channel $(\ell, j)$, $u_{cJ}(r)$ is the radial wave function of the valence electron, $\Theta_{cJ}(r)$ is the channel function, and $j + \ell = J$. Since the Hamiltonian is rotationally invariant, its eigenvalues are independent of the magnetic quantum number $M_J$, which will be omitted in the following.
In order to write the Schrödinger equation as a set of coupled-channel equations, the potential $V(r, \theta)$ in Eqs. (2 - 6) is expanded in multipoles:

$$V(r, \theta) = \sum_{\lambda} V_{\lambda}(r) P_{\lambda}(\cos \theta),$$  

(11)

where $V_{\lambda}(r)$ is the radial form factor and

$$P_{\lambda}(\cos \theta) = \frac{4\pi}{2\lambda + 1} Y_{\lambda}^{(\text{mod})}(\hat{\theta}) \cdot Y_{\lambda}^{(c)}(\hat{r}).$$  

(12)

The matrix elements $\langle \Theta^I_{\ell,j,c} | P_{\lambda}(\cos \theta) | \Theta^J_{\ell',j',c} \rangle$ are obtained by means of the standard angular momentum algebra [39]. The resulting coupled-channel equations for the radial wave functions $u_{c}'(r)$ can be written as:

$$\left[ \frac{d^2}{dr^2} - \frac{\ell_c(\ell_c + 1)}{r^2} - \frac{j_c(j_c + 1)}{I} + E_J \right] u_{c}'(r) = \sum_c V_{cc'}(r) u_{c'}(r),$$  

(13)

where $E_J$ is the energy of the system and

$$V_{cc'}(r) = \sum_{\lambda} \langle \Theta^I_{\ell,j,c} | P_{\lambda}(\cos \theta) | \Theta^J_{\ell',j',c} \rangle V_{\lambda}(r)$$  

(14)

is the coupling potential. Due to an $r^6$ dependence of the wave functions $u_{c}'(r)$ and $V(r, \theta)$ in Eqs. (6) and (7), the resulting pseudopotential is non-dilatation-antilocal.

**IV. BERGGREN EXPANSION METHOD**

The Berggren expansion method for studies of the bound states of dipolar anions has been introduced in Ref. [39]. In this method, the Hamiltonian is diagonalized in a complete basis of single-particle (s.p.) states, the so-called Berggren ensemble [41–43] which is generated by a finite-depth spherical one-body potential. The Berggren ensemble contains bound $(b)$, decaying $(d)$, and scattering $(s)$ single-particle states along the contour $\mathcal{L}_{\ell,j}$ for each considered partial wave $(\ell, j)$. For that reason, the Berggren ensemble is ideally suited to deal with weakly-bound and unbound structures having large spatial extensions, such as halos, Rydberg states, or decaying resonances. For more details and recent applications of BEM in the many-body context, see Ref. [75] and references cited therein.

While the finite-depth potential generating the Berggren ensemble can be chosen arbitrarily, to improve the convergence we take the diagonal part of the channel coupling potential $V_{cc'}(r)$. Indeed, since all basis states of a channel $c$ have the same values of $\ell_c$ and $j_c$, changing their generating potential only amounts to applying a unitary transformation. Hence, the most optimal potential is that for which all coupling between states of a given channel $c$ vanish, which is the case for $V_{cc}(r)$. The basis states $\Phi_{k,c}(r)$ are eigenstates of the spherical potential $V_{cc}(r)$, which are regular at origin and meet outgoing $(b, d)$ and scattering $(s)$ boundary conditions. Note that the wave number $k$ characterizing eigenstates $\Phi_{k,c}(r)$ is in general complex. The normalization of the bound states is standard, while that for the decaying states involves the exterior complex scaling [39, 75–78]. The scattering states are normalized to the Dirac delta function.

To determine Berggren ensemble, one calculates first the s.p. bound and resonance states of the generating s.p. potential for all chosen partial waves $(\ell, j)$. Then, for each channel $(\ell, j)$, one selects the contour $\mathcal{L}_{\ell,j}$ in a fourth quadrant of the complex $k$-plane. All $(\ell, j)$-scattering states in this ensemble belong to $\mathcal{L}_{\ell,j}$. The precise form of $\mathcal{L}_{\ell,j}$ is unimportant providing that all selected s.p. resonances for a given $(\ell, j)$ lie between this contour and the real $k$-axis for Re($k$) > 0. For each channel, the set of all resonant states and scattering states on $\mathcal{L}_{\ell,j}$ forms a complete s.p. basis.

In the present study, each contour $\mathcal{L}_{\ell,j}$ is composed of three segments: the first one from the origin to $k_{\text{peak}}$ in the fourth quadrant of the complex $k$-plane, the second one from $k_{\text{peak}}$ to $k_{\text{middle}}$ on the real $k$-axis (Re($k$) > 0), and the third one from $k_{\text{middle}}$ to $k_{\text{max}}$ also on the real $k$-axis. In all practical applications of the BEM, each contour $\mathcal{L}_{\ell,j}$ is discretized and the Gauss-Legendre quadrature is applied. The cutoff momentum $k = k_{\text{max}}$ should be sufficiently large to guarantee the completeness to a desired precision. The discretized scattering states $|\Phi_{n,c}\rangle$ are renormalized using the Gauss-Legendre weights. In this way, the Dirac delta normalization of the scattering states is replaced by the usual Kronecker delta normalization. In this way, all $|\Phi_{c}\rangle$ states can be treated on the same footing in the discretized Berggren completeness relation:

$$\sum_{i=1}^{N} |\Phi_{i,c}\rangle \langle \Phi_{i,c}| \simeq 1,$$  

(15)

where the $N$ basis states include bound, resonance, and discretized scattering states for each considered channel $c$.

The Hamiltonian matrix can be computed straightforwardly in the discretized Berggren basis [79]. The diagonal matrix elements are:

$$\langle \Phi_{i,c} | H | \Phi_{i,c} \rangle = \left( k_{i}^2 + \frac{j_{i}(j_{i} + 1)}{I} \right).$$  

(16)

To compute off-diagonal matrix elements, we apply the exterior complex scaling [53, 78, 80, 81]:

$$\langle \Phi_{i',c'} | H | \Phi_{i,c} \rangle = \langle \Phi_{i',c'} | V | \Phi_{i,c} \rangle =$$

$$= \int_{0}^{R} \Phi_{i',c'}(r) V_{cc'}(r) \Phi_{i,c}(r) dr$$

$$+ \sum_{ss' = \pm} \int_{0}^{+\infty} \Phi_{i',c'}^{(s')}(z(x)) V_{cc'}(z(x)) \Phi_{i,c}^{(s)}(z(x)) e^{i\theta} dx,$$

where $z(x) = R + xe^{i\theta}$, $\Phi_{i,c}(r)$ is the outgoing/incoming part of $\Phi_{i,c}(r)$, $\theta$ is a complex rotation angle chosen ac-
cording to the asymptotic behavior of $\Phi_{i,c}^{(\pm)}(r)$. The radius $R$ is chosen sufficiently large so that the exponentials of Eqs. (6) and (7) can be suppressed in the real asymptotic region. Since the coupling potential $V_{cc'}(r)$ in Eq. (17) decreases at least as fast as $r^{-2}$ in the complex plane, no singularities occur. Due to the completeness of the Berggren ensemble, the representation of the Hamiltonian by the matrix (16,17) is exact, up to contour discretization and momentum truncation.

V. PARAMETERS OF THE BEM CALCULATION

The parameters of the pseudo-potential for the HCN- anion are taken from Ref. [36]. These are:

- $\alpha_0 = 15.27 a_0^3$
- $\alpha_2 = 1.08 a_0^6$
- $Q_{zz} = 3.28 e a_0^2$
- $I = 7.42 \times 10^4 m_e a_0^2$
- $r_0 = 4.4 a_0$
- $r_c = 3.071622666 a_0$
- $V_0 = 4.0 \text{ Ry}$
- $s = 2.04 a_0$

and $a = a_0$. The value of $r_c$ has been adjusted to reproduce the experimental ground state ($J^z = 0^+$) energy [25]: $E^{\exp}(0^+) = -1.1465789 \times 10^{-4} \text{ Ry}$. For the dipolar moment of the molecule, we take the experimental value $\mu = 1.174 ea_0$. In the following, we express $r$ in units of the Bohr radius $a_0$, $I$ in units of $m_e a_0^2$, and energy in Ry. The $J^z = 1^-$ band head energy is also known experimentally, $E^{\exp}(1^-) = -8.8198377 \times 10^{-5} \text{ Ry}$, but no adjustment of the model parameters has been attempted to fit the experimental value.

To achieve stability of bound-state energies, the BEM calculations were carried out by including all partial waves with $\ell \leq \ell_{\text{max}} = 9$ and taking the optimized number of points ($N_C = 165$) on the complex contour with $k_{\text{max}} = 6a_0^{-1}$ for each $J^z$. For all $(\ell, j)$ channels and all $J^z$-values, the complex contour $L_{\ell,j}^+$ is taken close to the real axis ($k_{\text{peak}} = 0.15 - i10^{-7}$, $k_{\text{middle}} = 1.0$, and $k_{\text{max}} = 6.0$; all in $a_0^{-1}$). Its precise form has been adjusted by looking at the convergence of bound state energies when changing the imaginary part of $k_{\text{peak}}$. Each segment of any contour $L_{\ell,j}^+$ is discretized with the same number of points ($N_{C}/3 = 55$).

VI. IDENTIFICATION OF THE RESONANCES

The diagonalization of a complex-symmetric Hamiltonian matrix in BEM yields a set of eigenenergies which are the physical states (poles of the resolvent of the Hamiltonian) and a large number of complex-energy scattering states. The resonances are thus embedded in a discretized continuum of scattering states and their identification is not trivial [82, 83].

The eigenstates associated with resonances should be stable with respect to changes of the contour [82, 83]. Moreover, their dominant channel wave functions should exhaust a large fraction of the real part of the norm. The norm of an eigenstate of the Hamiltonian is given by:

$$\sum_c \sum_i |\Phi_{k,c} u_c|^2 = \sum_c n_c = 1,$$

where $n_c$ the norm of the channel wave function. In general, the norms of individual channel wave functions for resonances are complex numbers and their real parts are not necessarily positive definite. It may happen that if a large number of weak channels $\{c_i\}$ with small negative norms $\text{Re}(n_{c_i}) < 0$ contribute to the resonance wave function, then the dominant channel $c$ can have a norm $n_c > 1$. This does not come as a surprise as the channel wave functions have no obvious probabilistic interpretation.

To check the stability of BEM eigenstates, we varied the imaginary part of $k_{\text{peak}}$ from 0 to $-0.0001a_0^{-1}$ in all partial-wave contours. Resulting contour variations change both real $\Delta \text{Re}(E) \ll \text{Re}(E)$ and imaginary $\Delta \text{Im}(E)$ parts of the eigenenergies. The preci-

<table>
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<th>$\delta \text{Re}(E)$</th>
<th>$\text{Im}(E)$</th>
<th>$\delta \text{Im}(E)$</th>
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range \([0.001, 0.3]\) for the resonance states. As an example, the eigenvalues of \(J^\pi = 2^+\) resonant states are listed in Table I. It is seen that the relative variations of eigenenergies when changing the contour is shown in Fig. 1. One can see that the non-resonant states do not exhibit the degree of stability that is typical of resonant states. It is interesting to notice that several resonant states are found fairly away from the region of non-resonant eigenstates. The stability of resonant eigenstates persists if the real part of \(k_{\text{peak}}\) is varied from \(0.14 a_0^{-1}\) to \(0.16 a_0^{-1}\). In this case, the relative variations of the real part of the eigenstate energies dominate as can be seen in Fig. 2 for the two near-threshold resonances labeled 2 and 3 in Table I.

In order to demonstrate that the identified resonances are stable with respect to \(\ell_{\text{max}}\), in Fig. 3 we show the energy convergence for states 1-3 of Table I. In general, \(\text{Im}(E)\) is significantly more sensitive than \(\text{Re}(E)\) with respect to the addition of channels with higher \(\ell\)- and \(j\)-values. It is seen that \(\text{Im}(E)\) for resonances with the dominant channels \((\ell = 4, j = 4)\) and \((\ell = 3, j = 1)\) are converged already for \(\ell_{\text{max}} \geq 6\). The convergence for the narrow resonance with the dominant channel \((\ell = 2, j = 4)\) shown in Fig. 3(a) is also excellent, considering that in this case \(\text{Im}(E)\) is of the order of \(10^{-10}\) Ry, which is close to the limit of a numerical precision of our BEM calculations.

\[\text{Re}(E)\text{ are always smaller than }1\text{%}, \text{ while the relative variations of } \text{Im}(E)\text{ can reach } \sim 15\text{%}. \text{ Moreover, values of } \Delta \text{Im}(E)/\text{Im}(E)\text{ for different resonant states can differ by three orders of magnitude. In general, a better stability of the BEM eigenstates and, i.e., smaller values of } \Delta \text{Im}(E)/\text{Im}(E)\text{, is found for those eigenstates, which have several channel wave functions contributing significantly to the total norm. A typical accumulation}\]

\[\text{VII. INTRINSIC DENSITY}\]

It is instructive to present the density of the valence electron in the body-fixed frame. This can easily be done in the strong coupling scheme of the particle-plus-rotor model \([84–86]\), which is usually formulated in the \(K\)-representation associated with the intrinsic frame. Here, \(K_J = K_{\ell} + K_j\) is the projection of the total angular momentum on the symmetry axis of the molecule. Of particular interest is the adiabatic limit of \(I \to \infty\), where all
$J^\pi$ members of a rotational band collapse at the bandhead, i.e., they all can be associated with one intrinsic configuration. The $K$-representation is useful to visualize wave functions, group states with different $J$-values into rotational bands, and interpret the results in terms of Coriolis mixing [47, 50, 87–90].

In the body-fixed frame, the density of the valence electron in the state $J^\pi$ is axially-symmetric and can be decomposed as:

$$\rho_J(r, \theta) = \sum_{KJ} \rho_{JKJ}(r, \theta),$$  \hspace{1cm} \text{(19)}$$

where $(r, \theta)$ stand for the polar coordinates of the electron in the intrinsic frame, and the $K_J$-components of the density are:

$$\rho_{JKJ}(r, \theta) = \sum_{\ell, \ell'} \sum_j \frac{2j + 1}{2J + 1} \langle \ell K_J j 0 | J K_J \rangle \langle \ell' K_J j 0 | J K_J \rangle \times \frac{u^*_{\ell J}(r) u_{\ell' J}(r)}{r} Y_{\ell K_J}^{*}(\theta, 0) Y_{\ell' K_J}^{K J J}(\theta, 0).$$ \hspace{1cm} \text{(20)}$$

If all $K_J$-components except one vanish in Eq. (19), the adiabatic strong-coupling limit is reached and $K_J$ becomes a good quantum number. In this particular case, $\rho_{JKJ}$ can be identified as the intrinsic electronic density in the dipole-fixed reference frame. To quantify the degree of $K_J$-mixing, it is convenient to introduce the normalization amplitudes:

$$n_{JKJ} = \sum_{\ell, \ell'} \frac{2j + 1}{2J + 1} \langle \ell K_J j 0 | J K_J \rangle^2 \int |u_{\ell J}(r)|^2 dr.$$ \hspace{1cm} \text{(21)}$$

Due to (18), $n_{JKJ}$ fullfill the normalization condition:

$$\sum_{KJ} n_{JKJ} = 1.$$ \hspace{1cm} \text{(22)}$$

**VIII. RESULTS OF BEM CALCULATIONS**

Predicted energy spectra of HCN$^-$ with $J^\pi = 0^+, 1^-, 2^+, 3^-, 4^+$ and $5^-$ are shown in Table II. One may notice that the calculated energy of the $1^-$ bandhead, $E(1^-) = -8.96 \times 10^{-5}$ Ry, is close to the experimental value $E^{\exp}(1^-) = -8.82 \times 10^{-5}$ Ry. Moreover, consistently with earlier Refs. [25, 36], we do not find a $J^\pi = 3^-$ bound state.

The states listed in Table II are plotted in Fig. 4 in the complex energy plane. These states can be assembled according to their decay widths into five groups labelled $g_0$ to $g_4$. The group 4 contains bound states and very narrow threshold resonances of the dipolar anion. Narrow resonances are contained in groups 3 and 2 while broader states form groups 1 and 0. The characterization of the resonance spectra of HCN$^-$ in terms of groups $g_0$-$g_4$ will be provided below.

![FIG. 4. (Color online) Predicted energies of the HCN$^-$ dipolar anion for $J^\pi = 0^+, 1^-, 2^+, 3^-, 4^+$, and $5^-$ states in the complex-energy plane. Based on their complex energies, these states can be organized into five groups labelled $g_0$ to $g_4$. Bound states and near-threshold resonances belonging to $g_4$ and narrow resonances of $g_3$ are shown in the insert.]

![FIG. 5. (Color online) The intrinsic density of the valence electron in HCN$^-$ in the ground-state rotational band $J^\pi = 0^+_1, 1^-_1, 2^+_1, 3^-_1, \ldots$. (All densities are in $a_0^{-1}$.)]
TABLE II. Predicted complex energies (in Ry) of bound and resonance $0^+, 1^-, 2^+, 3^+, 4^+$, and $5^-$ states of the HCN⁻-dipolar anion. Numbers in the parentheses denote powers of 10.

<table>
<thead>
<tr>
<th>state</th>
<th>$E(0^+)$</th>
<th>$E(1^-)$</th>
<th>$E(2^+)$</th>
<th>$E(3^-)$</th>
<th>$E(4^+)$</th>
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<tr>
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that the members of the ground-state rotational band are practically degenerate in the adiabatic limit.

Figure 5 illustrates the intrinsic density for the ground-state band in the adiabatic limit ($I \to \infty$; $K_J = 0$). The intrinsic densities for all band members are numerically identical even though the associated wave functions in the laboratory system are different, see Fig. 6. The strongly asymmetric shape of electron’s distribution reflects the attraction/repulsion between the electron and positive/negative charge of the dipole (for other illustrative examples, see Refs. [5, 7, 11, 25, 91]).

We found that the density representation given by Eq. (19) can also be useful in the non-adiabatic case, with finite moment of inertia, to assign members of rotational bands. This is illustrated in Fig. 7 which shows the density (19) for the bound states $J^\pi = 0^+$, $1^-$, and $2^+$ of HCN⁻. Despite the fact that the strong coupling limit does not strictly apply in this case, distributions are practically identical and close to the intrinsic density displayed in Fig. 5.

B. Rotational bands

Excitation energies of the lowest-energy resonant (i.e., bound and resonance) states are plotted in Fig. 8 as a function of $J(J+1)$. The $J^\pi = 0^+$, $1^-$, $2^+$ bound states form a $K_J = 0$ rotational band as evidenced by their intrinsic densities shown in Fig. 7. Another $K_J = 0$ rotational band is built upon the $0^+_2$ resonance. According to Table II, a $1^-_2$ member of this band has a decay width that is reduced by over three orders of magnitude as compared to that of the $0^+_2$ bandhead. We predict other very narrow resonances as well. Among them, the $2^+_4$ state has $K_J = 2$ while $1^-_4$ and $2^+_5$ resonances have a mixed character.

As can be judged by results displayed in Fig. 8, except for few states with well defined $K_J$-values, majority of resonances are strongly $K_J$-mixed. Consequently, an identification of other rotational bands in the continuum, based on the concept of intrinsic density, is not straightforward. This is true, in particular for the supposed higher-$J$ members of the ground-state band. Figure 9 shows $\rho_{JKJ=0}$ for $J^\pi = 3^-_1$, $4^+_1$, $5^-_1$ resonances, which are expected – based on energy considerations – to form a continuation of the ground state rotational band. One can see that these densities are not only drastically different from those of $0^+_1$, $1^-_1$, and $2^+_1$ states but also change from one state to another. It is also worth noting that the densities of $3^-_1$, $4^+_1$, and $5^-_1$ resonances have spatial extensions that are dramatically larger as compared to
FIG. 6. (Color online) Channel wave functions \((\ell,j)\) of the \(J^\pi = 0^+\) (a) and \(4^+\) (b) members of the ground-state rotational band in HCN\(^-\) in the adiabatic limit.

the three bound members of the ground-state band.

As seen in Fig. 4, there appear clusters of resonances having the same total angular momentum \(J\) within one group \(g_i\). In each cluster, dominant channel wave functions have the same orbital angular momentum of the valence electron \(\ell\), but different rotational angular momenta of the molecule \(j\). Excitation energies of resonances are plotted as a function of the molecular angular momentum \(j\) in Fig. 10 for different groups of resonances of Fig. 4. It is seen that these states form very regular rotational band sequences in \(j\) rather than in \(J\). Different members of such bands lie close in the complex energy plane and have similar densities \(\rho_{JKJ}(r,\theta)\). This is illustrated in Fig. 11, which shows \(\rho_{JKJ}(r,\theta)\) for the two \(J^\pi = 5^-\) resonances marked by arrows in Fig. 10(c); namely \(5_5^-\), having the dominant parentage \((\ell,j) = (6,1)\), and \(5_{23}^-\), having the dominant parentage \((6,11)\).

The results of Fig. 10 suggest that the rotational resonance structures are governed by a weak \(\ell-j\) coupling, whereby the orbital motion of a valence electron is decoupled from the rotational motion of a dipolar neutral molecule. To illustrate the weak coupling better, in Fig. 12 we display the rotational bands of Fig. 10 with respect to the rigid rotor reference \(j(j + 1)/2I\). In the case of a perfect \(\ell-j\) decoupling, the rescaled energy in Fig. 12 should be equal to 1. One can see that this limit is reached in most cases, with deviations from unity being less than 10 \%. Larger deviations are found for few low-\(j\) states in bands with \(J = 2\) in \(g_2\) and \(J = 5\) in \(g_4\). Consequently, intrinsic densities for resonances in these two bands exhibit certain differences, whereas they are almost identical for bands close to the weak-coupling limit.

The variations seen in Fig. 12 can be traced back to the leading channel components along a \(j\)-band. Table III displays the leading channel wave functions to the resonances in different groups \(g_i\). Not surprisingly, the resonances forming \(j\)-band structures are associated with high orbital angular momentum components \(\ell = 6 - 9\) for which the centrifugal force induces a strong decoupling of the electron and the rotor. For regular bands
in Fig. 12, the ℓ-content is almost constant as a function of \(j\). For instance, for the four \(J = 5\) states in \(g_1\), the \((\ell,j)\) parentages of the two largest \((6,j)/(7,j+1)\) components are: 0.64/0.37 (\(j = 5\)), 0.67/0.36 (\(j = 7\), 0.69/0.35 (\(j = 9\)), and 0.70/0.34 (\(j = 11\)). On the other hand, for bands that exhibit stronger \(j\)-dependence in Fig. 12 the \(ℓ\)-compositions change.

Interesting complementary information about the arrangement of resonances in the continuum of HCN− can be seen in Fig. 13 which shows the decay width for various \(j\)-bands in different groups \(g_i\) and different total angular momenta \(J\) within a given group. One can see that the bands that exhibit largest deviations from the weak-coupling limit in Fig. 12 also show strong in-band variations of the decay width. In regular bands belonging to \(g_0\), \(g_1\), and \(g_3\), the width stays constant or slightly increases with \(j\). On the other hand, the irregular bands in \(g_2\) and \(g_4\) exhibit a decrease of \(Γ_J\) with \(j\). Such a behavior of lifetimes can be traced back to variations of the \((\ell,j)\)-content of the resonance wave function with rotation.

**IX. CONCLUSIONS**

In this work, we studied bound and resonance states of the dipole-bound anion of hydrogen cyanide HCN− using an open-system quantum-mechanical approach: the Berggren expansion method. To identify the decaying resonant states and separate them from the scattering background, we adopted the algorithm based on contour shift in the complex energy plane. To characterize spatial distributions of valence electrons, we introduced the intrinsic density of the valence electron. This quantity is useful when assigning resonant states into rotational bands.
Dipole molecules contain large numbers of electrons and this makes ab-initio treatments difficult. However, since we are interested in a description of a near-threshold spectrum of an anion rather than the whole molecular spectrum, we use a phenomenological approach based on a pseudo potential, with few parameters adjusted to experiment. This guarantees that all important reaction thresholds are described correctly, and this is essential for the description of one-electron continuum. The use of a pseudo-potential is well justified by a scale separation between the slow s.p. motion of the attached electron (comparable with rotational excitations of the molecule) and fast s.p. motion of HCN electrons. Such a mismatch of scales, well known in the field of quantum halos, guarantees the validity of an effective interaction treatment \cite{68–70}. The low ionization energy implies that the familiar Born-Oppenheimer approximation breaks down so the motion of the valence electron is highly non-adiabatic.

Since the pseudo-potential used is non-dilatation-analytic, it cannot be treated by a complex-coordinate method. Hence, available methods to treat this type of problems reduce to two classes of models. The first class of models can be associated with CESE \cite{63, 64}, where Hamiltonian coordinates are not complex-rotated and its eigenfunctions are split in two parts, an inner localized part and an outer part of outgoing character. Exterior complex scaling can thus be applied to the wave function in order to make it normalizable. The second class of models concerns BEM, where Hamiltonian coordinates remain real and the exterior complex scaling is utilized, but which is based on a diagonalization procedure using non-localized basis; this implies that the asymptotic form of eigenfunctions is not predefined and comes naturally from the configuration mixing. While both methods are theoretically equivalent, imposition of the outgoing asymptotics would be difficult in the studied case of HCN$^-$ anion. Indeed, due to the slowly decaying dipole potential, exponential asymptotic is attained only at distances of tens of thousands of $a_0$.

Non-adiabatic coupled-channel calculations with a pseudo potential adjusted to ground-state properties of...
HCN\(^-\) predict only three bound states of the dipole-bound anion: \(0^+, 1^-,\) and \(2^+\). Those states are members of the ground-state rotational band. The lowest \(3^+_1\) state is a threshold resonance; its intrinsic structure is very different from that of \(0^+_1, 1^+,\) and \(2^+_1\) states, and the lowest-energy resonances \(4^+_1,\) and \(5^+_1\).

The dissociation threshold in the HCN\(^-\) dipolar anion defines two distinct regimes of rotational motion. Below the threshold, rotational bands in \(J\) can be associated with bound states. Here, the valence electron follows the collective rotation of the molecule. This is not the case above the threshold where the motion of a valence electron in a resonance state is largely decoupled from the molecular rotation with the families of resonances forming regular band sequences in \(j\). Widths of resonances forming \(j\)-bands depend primarily on the electron’s orbital angular momentum in the dominant channel and remain fairly constant within each band for regular bands. Small irregularities in moments of inertia and decay width are predicted for very narrow resonances in the vicinity of the dissociation threshold.

In summary, this work demonstrates the feasibility of accurate calculations of weakly bound and unbound states of the dipolar anions using a non-adiabatic pseudo-potential method and the Berggren expansion approach. Our prediction of two distinct modes of rotation in this open quantum system awaits experimental confirmation. It is interesting to note a similarity between the problem of a dipolar anion and a coupling of electrons in high molecular Rydberg states to molecular rotations [92, 93]. Namely, in both cases one deals with non-adiabatic coupling of a slow electron to the fast rotational motion of the core, with no separation in the single-particle and collective time scales.

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