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Binding nonpolar molecules in an attractive inverse square potential

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The existence of stable orbital motion in a static attractive inverse square potential is predicted for nonpolar molecules with anisotropic polarizability interacting with a charged nanotube or nanowire. A simple three-degree-of-freedom model is constructed to illustrate the underlying physics and the binding characteristics. Numerical results using the diatomic molecule I_2 as an example are also presented.

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I. INTRODUCTION

The centrifugal potential of a central field is one well-known example of a repulsive inverse square $(1/R^2)$ potential. Much less familiar is the attractive inverse square $(-1/R^2)$ potential that can either overcome or exactly compensate a centrifugal barrier at all distances. Except for a zero-measure stable orbit with zero total energy a classical point particle in a $-1/R^2$ potential will either collapse to $R=0$ or escape from the potential field [1]. Quantum mechanically, a static $-1/R^2$ potential for a point particle does not support any bound states [1].

A nonpolar but polarizable neutral particle subject to the electric field of a charged nanowire or nanotube experiences a cylindrical $-1/R^2$ potential [2], hence interest in the $-1/R^2$ potential has grown considerably in recent years. It is believed that understanding and controlling the collapse and escape dynamics associated with a $-1/R^2$ potential will be important for describing the scattering and adsorption of atoms and molecules by charged nanowires or nanotubes [3], for seeking future nanoscale building blocks for atom optics and molecular optics, and for designing new atomic and molecular traps and storage rings with nanostructures. We note that the main features of the attractive inverse square potential have been experimentally observed using cold atoms interacting with a charged nanowire [4], and Ristroph *et al.* have proposed using a charged nanotube for high-efficiency single-atom detection [5].

The subject of this short paper is the orbital motion of *nonpolar molecules* in a $-1/R^2$ potential generated by a charged nanowire or nanotube (only nanowire will be mentioned hereafter). The anisotropic molecular polarizability induces a coupling between the molecular rotation dynamics and molecular orbital motion. These motions have very different characteristic time scales, hence their coupling can be treated as adiabatic. As shown below with a simple three-degree-of-freedom model, the resulting adiabatic effective potential can significantly deviate from the inverse square potential and, under certain conditions, can have a local minimum whose location is sensitively dependent on the orbital angular momentum, molecular rotational state, and the charge density of the nanowire. Our calculations lead to the prediction of long-lived, state-selective, and tunable binding of nonpolar molecules by a charged nanowire. A molecule being tens or even thousands of nanometers away from, but stably moving around, a charged nanowire is an intriguing state of motion that suggests possible construction of a storage ring for nonpolar molecules.

II. MODEL HAMILTONIAN

We consider a nonpolar but polarizable linear molecule with zero electronic angular momentum interacting with a nanowire carrying static charge Q per unit length. This uniform charge distribution assumption is appropriate for our model, as shown by a recent experiment using single-walled carbon nanotubes [6]. To construct a simple model we assume that the nanowire, of infinite length, coincides with the z axis, and describe the molecular rotational motion by a planar rotor whose angular momentum is parallel to the z axis. Then the longitudinal motion of the molecule is separable from its transverse motion, and the latter experiences a cylindrical $-1/R^2$ potential,

$$V_I(R,\phi_1,\phi_2) \equiv -\xi_1/R^2 - \xi_2 \sin^2(\phi)/R^2, \tag{1}$$

where R denotes the transverse distance between the molecule and the z axis,

$$\xi_1 \equiv \alpha_\perp Q^2/8\pi^2\epsilon_0^2, \tag{2}$$

$$\xi_2 \equiv (\alpha_\parallel - \alpha_\perp)Q^2/8\pi^2\epsilon_0^2, \tag{3}$$

with $\alpha_\parallel$ and $\alpha_\perp$ being the molecular polarizability parallel to and perpendicular to the molecular axis [7] (without loss of generality, we assume below $\xi_2>0$), $\phi\equiv\phi_2-\phi_1$, with the position of the molecule given by $[R\cos(\phi_1), R\sin(\phi_1)]$ and the angle between the molecular axis and the y axis given by ϕ_2. Note that this interaction potential tends to align the molecule along different directions as ϕ_1 evolves. Higher-order effects, such as van der Waals interaction and multipole interactions due to charge redistribution induced by the molecule [8], have been neglected, a valid assumption if the molecule is far from the surface of the charged nanowire. The model Hamiltonian is then given by

$$H = P_R^2/2M + J^2/2I + L^2/2MR^2 + V_I, \tag{4}$$

where P_R is the momentum variable conjugate to R, J is the rotational angular momentum variable conjugate to ϕ_2, M and I are the mass and moment of inertia of the molecule, and L denotes the orbital angular momentum variable conjugate to ϕ_1. The competition between the centrifugal potential $L^2/2MR^2$ and the inverse square potential V_I is crucial for the associated collapse and escape dynamics of a molecule. The significant difference from the atomic case, though, is that the potential energy V_I can also flow into the rotational degree of freedom (DOF). This interesting feature and its implications are analyzed below using a classical effective potential picture. For discussions on a particular symmetry of the model Hamiltonian, please refer to the last paragraph of the next section.

III. CLASSICAL THEORY WITH AN ADIABATIC TREATMENT

To seek an effective potential for the R DOF, we first consider the change in the kinetic energy $P_R^2/2M$ (denoted ΔE_k) as the molecule moves from $R=+\infty$ to an arbitrary $R>0$. The conservation of the total energy of the system yields

$$-\Delta E_k = -\xi_1/R^2 + H_{ROT} - J_\infty^2/2I + L_\infty^2/2MR^2 + V_{\Delta L}, \quad (5)$$

where L_∞ and J_∞ denote the orbital and rotational angular momentum at $R=+\infty$,

$$H_{ROT} \equiv J^2/2I - \xi_2 \sin^2(\phi)/R^2 \quad (6)$$

is the Hamilton function responsible for the rotational dynamics of the molecule, and

$$V_{\Delta L} \equiv [(L_\infty + \Delta L)^2 - L_\infty^2]/2MR^2 \quad (7)$$

results from the angular momentum exchange $\Delta L(=-\Delta J = J_\infty - J)$ between the rotational and translational DOF's.

The H_{ROT} defined above appears to depend upon four dynamical variables J, R, ϕ_1, and ϕ_2. Because the rotational motion is in general orders of magnitude faster than the center-of-mass motion, it can be assumed that H_{ROT} adiabatically changes with the slow variables R and ϕ_1. In accord with the classical adiabatic theorem, the action associated with H_{ROT} is a constant of motion and it is then found that the value of H_{ROT}, denoted E_{ROT}, depends only on R. For $E_{ROT}<0$, i.e., bounded rotational motion, we have

$$\begin{aligned} J_b &= (1/\pi)\int_{\phi_a}^{\phi_b} d\phi\{2I[E_{ROT} + \xi_2 \sin^2(\phi)/R^2]\}^{1/2} \\ &= R\sqrt{8IE_{ROT}}E1[(\eta+1)/\eta]/\pi\sqrt{\xi_2} \\ &\quad + \sqrt{8I\xi_2}E2[(\eta+1)/\eta]/\pi R, \end{aligned} \quad (8)$$

where $\eta \equiv \xi_2/E_{ROT}R^2$, $0<\phi_a$, $\phi_b<\pi$ are the associated turning points of the molecular rotational dyanamics, J_b is the action, and

$$E1[x] = (\pi/2)\left(1 + \sum_{n=1}^{+\infty} x^n[(2n-1)!!/(2n)!!]^2\right) \quad (9)$$

and

$$E2[x] = (\pi/2)\left(1 - \sum_{n=1}^{+\infty} x^n[(2n-1)!!/(2n)!!]^2/(2n-1)\right) \quad (10)$$

are complete elliptic intergals of the first and second kind [9]. For $E_{ROT}>0$, i.e., unbounded rotational motion, we find

$$\begin{aligned} J_\infty &= 1/(2\pi)\int_0^{2\pi} d\phi\{2I[E_{ROT} + \xi_2 \sin^2(\phi)/R^2]\}^{1/2} \\ &= (2/\pi)\sqrt{2IE_{ROT}(1+\eta)}E2[\eta/(1+\eta)]. \end{aligned} \quad (11)$$

In obtaining Eq. (11) we have used the fact that J_∞ itself determines the constant rotational action. The boundary between bounded and unbounded rotational motion lies at $R=\sqrt{8I\xi_2}/\pi J_\infty$. One subtle point is that the rotational period associated with $E_{ROT}=0$ diverges and the adiabaticity assumption breaks down as the system crosses this boundary. Nevertheless, by construction the E_{ROT} in the unbounded and bounded cases can be continuously connected by imposing the condition $J_b = J_\infty$.

The $V_{\Delta L}$ term in Eq. (5) is an oscillating term. As an approximation we only consider its time average over one period T_{ROT} of the fast molecular rotation,

$$\bar{V}_{\Delta L}(R) \equiv \langle V_{\Delta L}\rangle = [-2L_\infty\langle\Delta J\rangle + \langle(\Delta J)^2\rangle]/2MR^2, \quad (12)$$

where

$$\langle x\rangle \equiv (1/T_{ROT})\int_0^{T_{ROT}} x\, dt. \quad (13)$$

While a detailed examination of the validity of this treatment is beyond the scope of this work, we note that our numerically exact results strongly support this treatment. Using Eqs. (8) and (11), one finds (see the Appendix)

$$\langle\Delta J\rangle = -J_b, \quad (14)$$

$$\langle(\Delta J)^2\rangle = J_b^2 + 2IE_{ROT} + 2I\xi_2E2[(\eta+1)/\eta]/\{R^2E1[(\eta+1)/\eta]\} \quad (15)$$

for $E_{ROT}<0$; and

$$\langle(\Delta J)^2\rangle = -J_\infty\langle\Delta J\rangle, \quad (16)$$

$$\langle\Delta J\rangle = J_\infty(-1 + \pi^2/\{4E1[\eta/(1+\eta)]E2[\eta/(1+\eta)]\}) \quad (17)$$

for $E_{ROT}>0$.

The effective potential for the R DOF can now be defined as

$$V_{eff}(R) \equiv -\langle\Delta E_k\rangle = V_{adia}(R) + \bar{V}_{\Delta L}(R), \quad (18)$$

where the adiabatic potential

$$V_{adia}(R) \equiv L_\infty^2/2MR^2 - \xi_1/R^2 + E_{ROT}(R) - J_\infty^2/2I, \quad (19)$$

with $E_{ROT}(R)$ satisfies Eqs. (8) or (11) (with $J_b = J_\infty$). Since the analytical properties of $V_{eff}(R)$ can be explicitly inferred from Eqs. (3)–(5), the existence or nonexistence of stable orbital motion of the molecule can be examined in terms of the existence, and if any, the properties of local minima of $V_{eff}(R)$. To that end we discuss below in detail two different regimes of E_{ROT}, (a) $-E_{ROT}\sim\xi_2/R^2$, and (b) $E_{ROT}\geqslant\xi_2/R^2$, both of which allow for a minimum of $V_{eff}(R)$. Note that for $E_{ROT}\sim 0$, it can be proved that $V_{eff}(R)$ does not have a minimum.

In regime (a), molecular rotational motion is deeply bounded: $(\phi_1-\phi_2)$ undergoes only small oscillations and the molecule is strongly aligned along the $\phi_1\pm\pi/2$ direction. In this case $(\eta+1)/\eta\sim 0$, $E1[x]$ and $E2[x]$ in Eq. (8) can be expanded to the zeroth order of $(\eta+1)/\eta$, and one finds that

$$E_{ROT}(R)\sim-\xi_2/R^2+J_\infty\sqrt{\xi_2/2I}/R. \tag{20}$$

Hence the adiabatic potential V_{adia} acquires a Coulomb-like repulsive component $J_\infty\sqrt{\xi_2/2I}/R$ in addition to the inverse square components. Further using Eq. (15) one obtains

$$V_{eff}(R)\approx d_{-1}/R-d_{-2}/R^2+d_{-3}/R^3-J_\infty^2/2I, \tag{21}$$

where

$$d_{-1}=J_\infty\sqrt{\xi_2/2I}, \tag{22}$$

$$d_{-2}=\xi_1+\xi_2-(L_\infty+J_\infty)^2/2M, \tag{23}$$

and

$$d_{-3}=J_\infty\sqrt{I\xi_2/2}/M. \tag{24}$$

If $d_{-2}>\sqrt{3d_{-1}d_{-3}}$, then $V_{eff}(R)$ has a minimum at $R_{\min}\approx 3d_{-3}/[d_{-2}+(d_{-2}^2-3d_{-1}d_{-3})^{1/2}]$. However, it can be easily proved that $R_{\min}<\sqrt{3I/M}$, i.e., no larger than the scale of the molecule itself. For example, in the case of a homonuclear diatomic molecule, $\sqrt{3I/M}=\sqrt{3}r_0/2$, where r_0 is the bond length. Hence the potential minimum of $V_{eff}(R)$ located at $R_{\min}$ is unphysical because it would be inside the charged nanowire. Clearly then, if a nonpolar molecule is strongly aligned by the interaction potential V_I, stable orbital motion of the molecule is not expected.

In regime (b), $\eta\sim 0$ and we expand $E2[\eta/(1+\eta)]$ in Eq. (11) to the second order of η, yielding

$$E_{ROT}(R)\approx J_\infty^2/2I-\xi_2/2R^2+I\xi_2^2/16J_\infty^2R^4. \tag{25}$$

Using similar expansions we obtain from Eq. (17)

$$\langle\Delta J\rangle\approx-\xi_2^2I^2/8J_\infty^3R^4. \tag{26}$$

Equation (12) then shows that $\bar{V}_{\Delta L}(R)$ scales with $1/R^6$ and is therefore negligible compared with E_{ROT}. This makes it clear that to order $1/R^4$ the effective potential V_{eff} is given by

$$V_{eff}(R)\approx V_{adia}(R)\approx-C_{-2}/R^2+C_{-4}/R^4, \tag{27}$$

with

$$C_{-2}=\xi_1+\xi_2/2-L_\infty^2/2M, \tag{28}$$

and

$$C_{-4}=I\xi_2^2/(16J_\infty^2). \tag{29}$$

Equation (27) reveals that in the large-R regime V_{adia} plays a decisive role in the dynamics and acquires a repulsive $1/R^4$ component due to the adiabatic coupling between the rotational and translational DOF's. If $C_{-2}>0$ this repulsive component leads to a potential minimum, with the associated equilibrium position located at

$$R_e\approx\sqrt{2C_{-4}/C_{-2}}, \tag{30}$$

the potential well depth given by

$$D_e\approx C_{-2}^2/4C_{-4}, \tag{31}$$

and the force constant given by

$$k_e=d^2V_{eff}(R_e)/dR^2\approx C_{-2}^3/C_{-4}^2. \tag{32}$$

The existence of stable orbits can therefore be predicted. As C_{-2} is a function of L_∞ and C_{-4} is a function of the rotational action J_∞, all the binding characteristics R_e, D_e, and k_e are state sensitive. Note also that R_e, D_e, and k_e are functions of the charge density Q. Hence one can, in principle, tune the binding characteristics by adjusting Q. In particular, given that ξ_1 and ξ_2 scale with Q^2, one finds that R_e scales with Q for those L_∞ scaling linearly with R_e. The associated k_e then scales with Q^{-2} and D_e scales with Q^0, indicating that the potential wells have similar depth but get wider as Q increases.

Before ending this section, we discuss an interesting issue related to the symmetry of the model Hamiltonian introduced in Sec. II. Clearly, if we change ϕ_1 to $\phi_1'=\phi_1+\pi/2$, and exchange $\alpha_\parallel$ and $\alpha_\perp$, then the model Hamiltonian remains unchanged. Hence our solutions should reflect this symmetry. This is indeed the case. In particular, if $\alpha_\parallel$ and $\alpha_\perp$ are exchanged, then $\xi_1\rightarrow\xi_1'=\alpha_\parallel Q^2/(8\pi^2\epsilon_0^2)$, $\xi_2\rightarrow\xi_2'=-\xi_2$, and the rotational Hamilton function $H_{ROT}\rightarrow H_{ROT}'=J^2/2I-\xi_2'\sin^2(\phi')/R^2$, where $\phi'=\phi_2-\phi_1'$. Since $\xi_2'<0$, one cannot directly apply the above adiabatic treatment to H_{ROT}'. Instead, one should further split H'_{ROT} into

$$H_{ROT}'=-\xi_2'/R^2+H_{ROT}'', \tag{33}$$

where

$$H_{ROT}''=J^2/2I+\xi'_2\cos^2(\phi')/R^2=J^2/2I-\xi_2\sin^2(\phi)/R^2. \tag{34}$$

Our adiabatic treatment can then be applied to the $H_{ROT}''(R)$ term and the ϕ'-independent term ξ_2'/R^2 will make a new contribution to the adiabatic potential. It is then found that the total adiabatic potential seen by the R DOF is given by

$$V_{adia}'\equiv L_\infty^2/2MR^2-\xi_1'/R^2+E_{ROT}''(R)-J_\infty^2/2I-\xi_2'/R^2, \tag{35}$$

where $E_{ROT}''(R)$ denotes the value of H_{ROT}'' as the molecule adiabatically moves in space. Because $H_{ROT}''(R)$ takes the same functional form as H_{ROT} [see Eq. (6)], $E_{ROT}''(R)=E_{ROT}(R)$. Further using the fact $-(\xi_1'+\xi_2')=-\xi_1$, we obtain that $V_{adia}'(R)$ gives exactly the same potential as Eq.

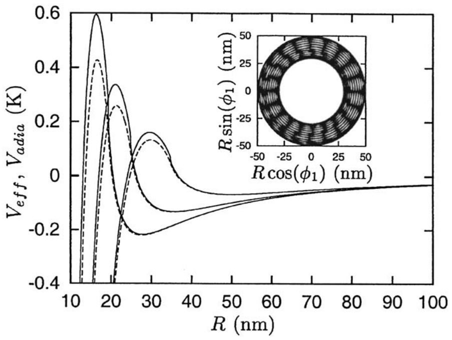

FIG. 1. Effective potential $V_{eff}(R)$ (solid line) obtained from Eq. (18) compared with the adiabatic potential $V_{adia}(R)$ (dashed line) obtained from Eq. (19), for $L_\infty = 2600\hbar$. From left to right $J_\infty = 9\hbar$, $7\hbar$, and $5\hbar$. See the text for other parameters that mimic the diatomic molecule I_2 moving around a charged nanowire. The inset shows a numerically exact classical trajectory in the case $J_\infty = 7\hbar$ for a duration of 1.0 μs. The pattern generated by the sample trajectory agrees with the classical effective potential analysis presented in Sec. III.

(19), a property expected from the symmetry of the model Hamiltonian.

IV. NUMERICAL EXAMPLE OF THE CLASSICAL DYNAMICS

As a numerical example of the classical dynamics we consider a set of system parameters that mimic the diatomic molecule $I_2 : \alpha_\parallel - \alpha_\perp = 6.69$ Å^3 and $\alpha_\perp = 8.0$ Å^3 [10], $I = 0.037\,37$ cm^{-1}, $M = 253.8$ a.m.u. ξ_2 is set to be 4000 K nm^2, corresponding to a charge density of 4.24 unit charge per nm. Figure 1 shows $V_{adia}(R)$ and $V_{eff}(R)$ for $L_\infty = 2600\hbar$ and $J_\infty = 5\hbar, 7\hbar, 9\hbar$. The asymptotic behavior of $V_{eff}(R)$ is seen to be the same for different J_∞, and $V_{adia}(R)$ is almost indistinguishable from $V_{eff}(R)$ in the potential-well region. These observations confirm Eq. (27). More importantly, the shape and location of the potential wells seen in Fig. 1 agree quantitatively with our theoretical results in terms of C_{-2} and C_{-4}. In addition, a comparison between the effective potentials shown in Fig. 1 suggests that rotational state manipulation can be used to switch between different bound orbits or between a bound orbit and a collapsing or escaping trajectory. Also shown in Fig. 1 is one typical bound orbit of 1.0 μs duration (which is about 30 times longer than the radial oscillation period $2\pi\sqrt{M/k_e}$) obtained from directly solving Hamilton's equation of motion. The pattern generated by the sample trajectory reflects the whereabouts of radial turning points and the frequency ratio between radial and angular motion. The numerically exact results obtained from classical trajectories totally agree with the effective potential picture presented above.

V. QUANTUM DYNAMICS

Our predictions and calculations so far have been based solely on classical dynamics. Consider now a direct quantization of our simple model Hamiltonian, i.e.,

$$[R, P_R] = [\phi_1, L] = [\phi_2, J] = i\hbar, \tag{36}$$

where $[\cdot]$ is the quantum commutator. Upon quantization the adiabatic evolution of the rotational energy $E_{ROT}(R)$ is related to the stationary Schrödinger equation parametrized by R, i.e.,

$$H_{ROT}|\psi\rangle = E(R)|\psi\rangle, \tag{37}$$

where ψ is understood to be a function of ϕ for each fixed R. That is, within the adiabatic treatment, the translational motion of the molecule is sufficiently slow as compared with the rotational motion, such that as R changes the rotational state of the molecule can adiabatically follow a particular family of eigenstates parametrized by R. However, as seen below, the adiabatic following of the quantum rotational state with R may lead to subtle consequences that are absent in the classical dynamics. In particular, the adiabatic states may no longer correlate with a single L_∞ (the orbital angular momentum at $R = \infty$) and hence the effective potential approach used in the classical analysis, which is always associated with a single value of L_∞, should be re-examined.

We first convert Eq. (37) to the familiar form of Mathieu's equation [9]:

$$d^2\psi/d\phi^2 + [a - 2q\cos(2\phi)]\psi = 0, \tag{38}$$

with

$$E(R) = (\hbar^2 a/2I - \xi_2/2R^2) \tag{39}$$

and

$$q = I\xi_2/2\hbar^2 R^2. \tag{40}$$

The eigenfunctions and eigenvalues of Mathieu's equation are well known. Let $|\psi^+_{J_\infty}\rangle$ and $|\psi^-_{J_\infty}\rangle$ be the even-parity and odd-parity eigenfunctions that adiabatically correlate with $(1/\sqrt{\pi})\cos(J_\infty\phi/\hbar)$ and $(1/\sqrt{\pi})\sin(J_\infty\phi/\hbar)$, respectively. The associated eigenvalues are denoted by $E^+_{J_\infty}(R)$ and $E^-_{J_\infty}(R)$. Using the characteristic values of Mathieu's equation, one finds that for large J_∞ and R (e.g., $J_\infty \geqslant 10\hbar$, $q \leqslant 10$), $E^+_{J_\infty}(R) \approx E^-_{J_\infty}(R)$. At first glance this seems to suggest an almost-degeneracy problem that precludes the adiabatic treatment of the rotational motion. This is certainly not true because otherwise quantum-classical correspondence would no longer exist. Specifically, cases of large J_∞ and R also belong to the regime where $E^+_{J_\infty}(R)$ and $E^-_{J_\infty}(R)$ assume, to order q^2, almost the same analytical form as $E_{ROT}(R)$ in Eq. (25) except that J^2_∞ is replaced by $(J^2_\infty - \hbar^2)$ [9]. Hence for large J_∞ and R the classical effective potential picture should apply. Motivated by this reasoning in the light of quantum-classical correspondence, one finds that for large J_∞ and large R a more reasonable representation for describing the quantum dynamics should be the superposition states

$$|+\tilde{J}_\infty\rangle \equiv (|\psi^+_{J_\infty}\rangle + i|\psi^-_{J_\infty}\rangle)/\sqrt{2},$$

$$|-\tilde{J}_\infty\rangle \equiv (|\psi^+_{J_\infty}\rangle - i|\psi^-_{J_\infty}\rangle)/\sqrt{2}, \tag{41}$$

where state $|+\tilde{J}_\infty\rangle$ adiabatically correlates with a freely rotating state with angular momentum J_∞ and state $|-\tilde{J}_\infty\rangle$ adiabatically correlates with a freely rotating state with angular momentum $-J_\infty$. A simple analog of this procedure is that the classical state of a particle moving freely with a certain momentum should be compared with a quantum eigenstate of the momentum operator, which is a superposition state of two degenerate eigenstates of the Hamiltonian. We can then construct the quasistationary quantum state of the entire model system as $\exp[iK\phi_1/\hbar]|\chi(R)\rangle|+\tilde{J}_\infty\rangle$ or $\exp[iK\phi_1/\hbar]|\chi(R)\rangle|-\tilde{J}_\infty\rangle$, where $\chi(R)$ is a quasi-bound state of the local minimum of $V_{eff}(R)$ and K is the conserved total angular momentum. At $R=\infty$, the constructed state $\exp[iK\phi_1/\hbar]|\chi(R)\rangle|+\tilde{J}_\infty\rangle$ $(\exp[iK\phi_1/\hbar]|\chi(R)\rangle|-\tilde{J}_\infty\rangle)$ describes a free rotor with rotational angular momentum J_∞ $(-J_\infty)$, and with a definite orbital angular momentum $K-J_\infty$ $(K+J_\infty)$. Indeed, this is why a single effective potential V_{eff}, associated with the asymptotic orbital angular momentum of $L_\infty=K-J_\infty$ $(L_\infty=K+J_\infty)$, and with the asymptotic rotational angular momentum J_∞ $(-J_\infty)$, can be used to account for the dynamics of the constructed state $\exp[iK\phi_1/\hbar]|\chi(R)\rangle|+\tilde{J}_\infty\rangle$ $(\exp[iK\phi_1/\hbar]|\chi(R)\rangle|-\tilde{J}_\infty\rangle)$. We call the states $\exp[iK\phi_1/\hbar]|\chi(R)\rangle|\pm\tilde{J}_\infty\rangle$ "quasi-stationary" because (a) any nonadiabatic transitions between $|+J_\infty\rangle$ and $|-J_\infty\rangle$ are neglected, and (b) states $|+J_\infty\rangle$ and $|-J_\infty\rangle$ are only approximate eigenstates of H_{ROT} before the quantum Rabi-like oscillations between them become appreciable [the oscillation period gets larger and larger as the splitting between $E^+_{J_\infty}(R)$ and $E^-_{J_\infty}(R)$ gets smaller and smaller].

For small J_∞ and large q the difference between the neighboring even-parity and odd-parity eigenstates of H_{ROT} becomes non-negligible and states $|\pm\tilde{J}_\infty\rangle$ no longer provide a good representation to construct quasi-stationary binding states due to the quantum oscillations between them. For these cases in the deep quantum regime, the classical dynamics no longer provides a reliable guide in understanding the dynamics. Indeed, because the total angular momentum is always conserved at K, the quantum oscillations between $|+\tilde{J}_\infty\rangle$ and $|-\tilde{J}_\infty\rangle$ imply that the orbital angular momentum L, and its asymptotic value L_∞, can also have a characteristic oscillation amplitude $2J_\infty$. This then suggests that the adiabatically evolving quantum state can be asymptotically correlated with different orbital angular momentum L_∞ and it becomes impossible to describe the dynamics by considering one particular effective potential $V_{eff}(R)$ or $V_{adia}(R)$ that is associated with one particular value of L_∞ [see Eqs. (18) and (19)]. As such, for observation times larger than $\hbar/[E^+_{J_\infty}(\bar{R})-E^-_{J_\infty}(\bar{R})]$, where $\bar{R}$ is the characteristic binding radius, a simple form of quasistationary state no longer exists and a single effective potential for fixed L_∞ and j_∞ will be insufficient to describe the quantum dynamics. We stress that this observation is unrelated to the possible nonadiabaticity associated with the rotation-vibration coupling, i.e., it holds even in the true adiabatic limit.

To gain more insight and help analyze the quantum results in the deep quantum regime, we now return to the $(|\psi^+_{J_\infty}\rangle,|\psi^-_{J_\infty}\rangle)$ representation and define a mean adiabatic potential for either $|\psi^+_{J_\infty}\rangle$ or $|\psi^-_{J_\infty}\rangle$, i.e.,

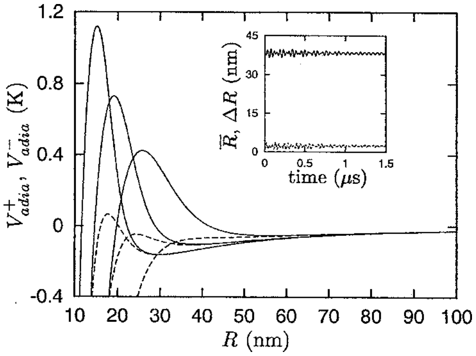

FIG. 2. $V^+_{adia}(R)$ (solid line) compared with $V^-_{adia}(R)$ (dashed line) for $L_\infty=2600\hbar$ [see Eq. (42) for the definition of $V^\pm_{adia}(R)$]. From left to right $J_\infty=9\hbar$, $7\hbar$, and $5\hbar$. Other parameters are the same as in the classical calculations. The splitting between V^+_{adia} and V^-_{adia} is large in the case of $J_\infty=5\hbar$, but is insignificant in the potential-well region for $J_\infty=7\hbar$, $9\hbar$. $(V^+_{adia}+V^-_{adia})/2$ is seen to qualitatively agree with the classical adiabatic potential $V_{adia}(R)$ shown in Fig. 1. The inset shows the long-lived binding of a quantum wave packet in the case $J_\infty=7\hbar$, in terms of the time dependence of $\bar{R}$ (upper curve) and ΔR (bottom curve), the mean value, and the variance of R.

$$V^\pm_{adia}(R) \equiv [(K-J_\infty)^2+(K+J_\infty)^2]/4MR^2 - \xi_1/R^2 + E^\pm_{J_\infty}(R) - J^2_\infty/2I. \tag{42}$$

This consideration is motivated by the fact that for fixed total angular momentum K and at $R=\infty$, state $|+\psi^+_{J_\infty}\rangle$ (the same for state $|-\psi^+_{J_\infty}\rangle$) must correlate with states with orbital angular momentum of $L_\infty=K_\infty+J_\infty$ and $L_\infty=K_\infty-J_\infty$ [hence the centrifugal potentials $(K-J_\infty)^2/2MR^2$ and $(K+J_\infty)^2/2MR^2$]. Within the adiabatic treatment, the wave-packet dynamics on different $V^\pm_{adia}(R)$ correlated with different $|J_\infty|$ are not coupled because an adiabatically evolving rotational state does not change its number of nodes. However, it can be proved that the two average potentials V^+_{adia} and V^-_{adia} are always coupled to each other. A simple proof of the intrinsic coupling between V^+_{adia} and V^-_{adia} lies in the properties of the operator L^2. Specifically, because the operator $L^2=(K-J)^2$ contain a term like $2K(d/d\phi)$ that is an odd function of ϕ, it is noncommutable with the parity operator associated with ϕ and therefore does not preserve the parity of the rotational eigenstates as functions of ϕ. From this analysis it becomes clear that the long-lived binding of a quantum wave packet necessarily requires that both V^+_{adia} and V^-_{adia} have a local minimum. For example, if V^+_{adia} has a local minimum but V^-_{adia} does not, then components of the system wave function can first "jump" from the V^+_{adia} surface to the V^-_{adia} surface and then escape from the nanowire or collapse to the center of the nanowire through V^-_{adia}. However, considering that the average potentials $V^\pm_{adia}$ are just one of many possible representations to interpret the quantum dynamics, it is not totally clear if both V^+_{adia} and V^-_{adia} having a local minimum is a sufficient condition for stable binding states.

Using the same system parameters as above, in Fig. 2 we show $V^\pm_{adia}$ for $L_\infty=2600\hbar$, $J_\infty=5\hbar,7\hbar,9\hbar$. It is seen that the splitting between V^+_{adia} and V^-_{adia} in the case of $J_\infty=5\hbar$ is dramatic insofar as V^-_{adia} does not have a minimum but V^+_{adia} does (this is a common feature for $\hbar \leqslant J_\infty \leqslant 5\hbar$). In cases of $J_\infty=7\hbar, 9\hbar$ the splitting is insignificant in the potential-well region. Interestingly, for all these cases with rather small J_∞, the average behavior of V^+_{adia} and V^-_{adia}, i.e., $(V^+_{adia}+V^-_{adia})/2$, still qualitatively agrees with the classical adiabatic potential V_{adia} shown in Fig. 1. It should also be noted that for larger L_∞ the classical value of R_e increases, q decreases, and the system gets closer to the classical limit. For example, for $L_\infty=2625\hbar$ both V^+_{adia} and V^-_{adia} have a minimum even in the case $J_\infty=5\hbar$.

Extensive quantum wave-packet dynamics calculations in parallel with our classical calculations have also been carried out. Initial quantum states were chosen to be a direct product of $\exp[iK\phi_1/\hbar], |\psi^+_{J_\infty}\rangle$ and the quasiground state associated with V^+_{adia}. Absorptive boundary conditions are applied to both the R grid and the P_R grid to account for any possible adsorption and escape probability. When $J_\infty=5\hbar$, $L_\infty=2600\hbar$, the quantum survival probability decreases at a considerable rate, consistent with the finding that V^+_{adia} has a minimum but V^-_{adia} does not. However, for all the other cases considered, i.e., $L_\infty=2625\hbar$, $J_\infty=5\hbar, 7\hbar, 9\hbar$, and $L_\infty=2600\hbar$, $J_\infty=7\hbar, 9\hbar$, long-lived binding of quantum wave packets is observed: numerically the quantum survival probability for a time interval of 1.5 μs is found to be $>99.999\%$. A typical quantum result displayed in Fig. 2 shows that the mean value and the variance of R associated with a time-evolving quantum state undergo only small-amplitude oscillations at all times. Our numerical results also directly demonstrate that the quantum tunneling out of a binding potential well can be neglected, thus justifying a classical picture of the translational motion. Indeed, a rough estimate should give that even for the rather shallow potential wells (dashed lines) shown in Fig. 2, the tunneling transmission coefficient is extremely small ($<\exp[-50]$) due to the relatively large mass of a molecule (e.g., as compared with that of an electron).

VI. CONCLUDING REMARKS

In conclusion, we have predicted a type of intriguing molecule-nanostructure binding state, thus opening up a different direction that is of considerable interest to nanoscale molecular physics. In particular, using a simple model we have predicted long-lived binding and the associated tunable binding characteristics for nonpolar molecules moving in a static attractive inverse square potential of a charged nanowire. Experimental studies of systems like our model should be possible with today's nanotechnology and molecular cooling technology. The adiabatic treatment developed in this work should be also useful in describing the cold collisions between nonpolar molecules and a charged nanowire. The stable molecule-nanostructure binding states might find applications in designing molecular traps and molecular storage rings, and provide an interesting setup for studying fundamental issues such as the quantum-classical correspondence principle on the mesoscopic scale. In future studies we plan to take into account all molecular degrees of freeom (thus lifting the "planar-rotor" approximation), and apply similar approaches to the dynamics of polar molecules in the field of a charged nanowire.

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APPENDIX: DERIVATION OF EQS. (14)–(17)

The oscillating term $V_{\Delta L}$ results from the angular momentum exchange between the molecular rotational and translational degrees of freedom. Consistent with the adiabatic treatment of the rotation-vibration coupling, we only consider its time average over one period T_{ROT} of the fast rotational motion [see Eqs. (12)–(17)]. Because the $V_{\Delta L}$ term is eventually neglected in the theoretical analysis, the results of Eqs. (14)–(17) will not directly help predict the characteristics of the molecule-nanostructure binding states. However, they are of theoretical interest in their own right [e.g., for understanding the difference between $V_{eff}(R)$ and $V_{adia}(R)$]. Here we present some details associated with the derivation of Eqs. (14)–(17).

Consider first the case of $E_{ROT}<0$. Then the rotational motion has two turning points denoted ϕ_a and ϕ_b. The rotational period T^b_{ROT} is given by

$$\begin{aligned} T^b_{ROT} &= 2\int_{\phi_a}^{\phi_b} \frac{dt}{d\phi} d\phi = 2I\int_{\phi_a}^{\phi_b} \frac{d\phi}{J} \\ &= 2I\int_{\phi_a}^{\phi_b} \frac{d\phi}{\sqrt{2IE_{ROT}[1+\eta\sin^2(\phi)]}} \\ &= \sqrt{8I/E_{ROT}}E1[(\eta+1)/\eta]/\sqrt{\eta}. \end{aligned} \tag{A1}$$

Because the rotational motion has turning points, J changes its sign over one period of motion. This directly leads to $\langle J\rangle=0$. It then follows that

$$\langle \Delta J\rangle \equiv \langle J - J_b\rangle = -J_b, \tag{A2}$$

which is identical with Eq. (14). Further,

$$\begin{aligned} \langle(\Delta J)^2\rangle &\equiv (\langle J - J_b)^2\rangle = J_b^2 + \langle J^2\rangle \\ &= J_b^2 + \frac{1}{T^b_{ROT}}\int_0^{T^b_{ROT}} J^2 dt \\ &= J_b^2 + \frac{I}{T^b_{ROT}}\int_0^{T^b_{ROT}} J d\phi \\ &= J_b^2 + \frac{2\pi J_b I}{T^b_{ROT}}, \end{aligned} \tag{A3}$$

where in the last step we have used the definition of the rotational action J_b. Now inserting the explicit expression of T^b_{ROT} in Eq. (A1) into the above result, we obtain

$$\langle(\Delta J)^2\rangle = J_b^2 + \frac{2\pi J_b I}{\sqrt{8I/\eta E_{ROT}}E1[(\eta+1)/\eta]}. \tag{A4}$$

Substituting the analytical expression of J_b [see Eq. (8)] into Eq. (A4), we obtain Eq. (15).

For the unbounded case, the rotational period T^u_{ROT} is given by

$$T^u_{ROT} = 2\int_0^{\pi} \frac{dt}{d\phi} d\phi = 4I\int_0^{\pi/2} \frac{d\phi}{\sqrt{2IE_{ROT}[1+\eta\sin^2(\phi)]}} = \sqrt{8I/E_{ROT}}E1[\eta/(1+\eta)]/\sqrt{(1+\eta)}. \tag{A5}$$

Using the definition of J_∞, i.e., $J_\infty \equiv 1/(2\pi)\int_0^{2\pi} J d\phi$, we have

$$\langle(\Delta J)^2\rangle = \frac{1}{T^u_{ROT}}\int_0^{T^u_{ROT}} (J-J_\infty)^2\, dt = \frac{2\pi J_\infty I}{T^u_{ROT}} + J^2_\infty - \frac{4\pi J_\infty I}{T^u_{ROT}} = J_\infty\left(J_\infty - \frac{2\pi I}{T^u_{ROT}}\right). \tag{A6}$$

Noticing that

$$\langle\Delta J\rangle = \left[\frac{1}{T^u_{ROT}}\int_0^{T^u_{ROT}} J\, dt\right] - J_\infty = \frac{2\pi I}{T^u_{ROT}} - J_\infty \tag{A7}$$

we immediately get Eq. (16) by comparing Eqs. (A6) and (A7). We then substitute Eq. (A5) into Eq. (A6), yielding

$$\langle(\Delta J)^2\rangle = J^2_\infty \frac{\pi J_\infty \sqrt{2IE_{ROT}(1+\eta)}}{2E1[\eta/(1+\eta)]}. \tag{A8}$$

Equation (A8) can be easily shown to be equivalent to Eq. (17), by making use of the expression of J_∞ shown in Eq. (11).

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