Sticking and desorption of hydrogen on graphite: A comparative study of different models

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We study the physisorption of atomic hydrogen on graphitic surfaces with four different quantum mechanical methods: perturbation and effective Hamiltonian theories, close coupling wavepacket, and reduced density matrix propagation methods. Corrugation is included in the modeling of the surface. Sticking is a fast process which is well described by all methods. Sticking probabilities are of the order of a few percent in the collision energy range 0–25 meV, but are enhanced for collision energies close to those of diffraction resonances. Sticking also increases with surface temperature. Desorption is a slow process which involves multiphonon processes. We show, however, how to correct the close coupling wavepacket method to account for such phenomena and obtain correct time constants for initial state decay. Desorption time constants are in the range of 20–50 ps for a surface temperature of 300 K. © 2011 American Institute of Physics. [doi:10.1063/1.3565446]

I. INTRODUCTION

The interaction of hydrogen atoms with graphene and graphite surfaces has been the subject of intense investigation in recent years. Numerous studies have been motivated by the erosion of graphite walls in fusion devices,^{1,2} and by the prospect of tuning the electrical properties of single layer graphene by controlled hydrogenation.³ In addition, it has been proposed that the large abundance of molecular hydrogen in the universe is a result of atomic hydrogen combining on interstellar dust grains,^{4,5} which are known to have graphitic components.⁶ It has been suggested that this reaction is of the Eley–Rideal-type, where an H atom in the gas phase collides and reacts with an H atom adsorbed onto the dust grain, forming H₂. It is also possible that two adsorbed H atoms could diffuse on the dust grain and react via a Langmuir–Hinshelwood mechanism. Both mechanisms require that one or more H atoms first stick to these dust grains. Electronic structure calculations have shown^{7,8} that when hydrogen chemisorbs onto a graphene/graphite surface, the carbon atom closest to the hydrogen puckers out of the plane of the surface, as a result of a change in the hybridization of the C orbitals from sp^2 to sp^3 . As a result of this lattice distortion, there is a barrier to chemisorption of the order of 0.2 eV. Thus, in the low energy regime characterizing cold interstellar media, chemisorption is energetically forbidden, and any adsorbed H is likely to be physisorbed, as there is no barrier to this process. The physisorption well is about

40 meV deep, and has been characterized by the selective adsorption resonances observed in experimental studies of hydrogen atom scattering from graphite,⁹ as well as recent, accurate electronic structure calculations.^{10,11} Two theoretical studies have estimated that the probability for sticking into this physisorption well at low energies is on the order of a few percent.^{12,13} However, for specific values of the incoming atom's energy, selective adsorption resonances can occur. Particles trapped near the surface in these long lived quasi-bound states can dissipate energy by exciting vibrations of the substrate, eventually sticking. For the case of hydrogen physisorption on graphite, it was predicted that the corrugation of the surface could lead to enhanced sticking via diffraction mediated selective adsorption.¹³ These trapped or stuck particles can diffuse on the substrate for some time, and engage in chemistry, until they eventually desorb, with a rate determined by the substrate temperature. Quantum scattering calculations have shown that the Eley–Rideal cross sections for H₂ formation are large for both chemisorbed and physisorbed H.¹⁴ Quantum scattering calculations have also shown that Langmuir–Hinshelwood cross-radii are large in the physisorption regime.¹⁵

The present paper has two objectives. One is to consider in more detail the effect of selective adsorption resonances on these trapping–sticking–desorption processes. Such a study was undertaken in Ref. 13 for the lowest energy resonance. The problem is studied here in a broader perspective encompassing higher energies, and we also examine the desorption process in more detail. A second objective is to take a closer look at different quantum mechanical approaches that can be used to model these complex trapping–sticking–desorption processes. We compare their ability to describe the different physical phenomena at play. We first consider a reduced

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density matrix (RDM) formalism,^{16–20} where the substrate is described as a phonon bath in constant equilibrium, and the Markov approximation is used. A short time propagator is derived in the weak coupling limit which allows one to model the whole trapping–sticking–desorption process even at long times, because the continuous exchange of energy between the surface and the trapped atom is described properly. A similar formalism was used in previous studies^{13,21} of light particles interacting with surfaces, but some improvements are presented in the present paper.

We then consider the close coupling wavepacket method (CCWP) (Refs. 22 and 23) already used to model the chemisorption of H on graphite.^{24,25} A wavefunction describing an atom incident on a thermally averaged substrate initial state is expanded in a product basis of phonon and atomic states. The phonon states are obtained from a discretized representation of the first Brillouin zone in reciprocal space. The coefficients in the expansion are solutions of a set of time dependent first-order differential equations. The main approximation in this method is the severe truncation of the phonon basis: only states involving a difference of zero or one phonon with respect to the initial thermally averaged occupation numbers are considered. This one-phonon approximation is appropriate for describing atoms interacting weakly on short time scales with substrates, but more problematic for stronger interactions. We will show here that in the present context, a possible remedy is to consider single one-phonon processes sequentially, allowing one to describe the whole trapping–sticking–desorption process with different CCWP calculations with different initial conditions. Given the low collision energies, the weak physisorption interaction, and the small H/C mass ratio, a weak coupling assumption is reasonable for this problem. Thus, perturbation theory (PT) should provide reasonable results and will also be considered here. This level of theory has been used in the context of vibrational relaxation on surfaces^{26,27} and is extended here to the collision context. We will show, however, that effective Hamiltonian (EH) theory (see for instance Ref. 28) provides some improvement to PT by allowing some feedback from sticking onto the collision process. Sec. II describes the methods implemented in this paper: RDM, CCWP, EH, and PT. Results concerning sticking and desorption are shown in Secs. III A and III B, respectively. Conclusion follows in Sec. IV.

II. METHODS

A. The Hamiltonian

We follow the formalism already described in Refs. 13 and 21 and focus mainly on the changes made for the present paper. The Hamiltonian of the system is $\mathbf{H} = \mathbf{K} + \mathbf{H}_b + V$, where $\mathbf{K}$ is the kinetic energy of the incoming hydrogen atom, and $\mathbf{H}_b$ is the Hamiltonian describing the vibration of the harmonic lattice. The interaction potential V is a complicated function of the coordinates of the lattice atoms, given by their displacements from equilibrium, $\{\mathbf{u}_i\}$, and the location of the incoming particle, $\mathbf{r} = (\mathbf{R}, z)$, where $\mathbf{R} = (x, y)$ is the atom's position projected onto the surface plane, and z is the atom's distance above this plane. In the absence of thermal fluctua-

tions, and laterally averaging the atom–substrate interaction over the corrugation, we define a flat frozen atom–substrate interaction potential $V_f(z)$ as a sum of a short range repulsive part, $\Delta(z)$, and a long range attractive part, $V_{\text{att}}(z)$:

$$V_f(z) = \Delta(z) + V_{\text{att}}(z). \quad (1)$$

We assume that corrugation and thermal fluctuations modify only the short range repulsive part, and write

$$V(\mathbf{r}, \{\mathbf{u}_i\}) = \Delta(z) (1 + 2\alpha W(\mathbf{R}, \{\mathbf{u}_i\})) + V_{\text{att}}(z). \quad (2)$$

At reasonable temperatures we can Taylor expand the modulation function $W(\mathbf{R}, \{\mathbf{u}_i\})$ to first-order in the lattice atom displacements $\{\mathbf{u}_i\}$, and separate the full Hamiltonian into a system part $\mathbf{H}_s$, a bath part $\mathbf{H}_b$, and a coupling between them, V_c . Thus, $\mathbf{H} = \mathbf{H}_s + \mathbf{H}_b + V_c$ with

$$\mathbf{H}_s = \mathbf{K} + V_s(\mathbf{r}), \quad (3)$$

$$V_s(\mathbf{r}) = \Delta(z) + V_{\text{att}}(z) + 2\alpha\Delta(z)W(\mathbf{R}, \mathbf{0}), \quad (4)$$

and

$$V_c(\mathbf{r}, \{\mathbf{u}_i\}) = 2\alpha\Delta(z) \sum_i \frac{\partial W(\mathbf{R}, \mathbf{0})}{\partial \mathbf{u}_i} \mathbf{u}_i. \quad (5)$$

The flat-surface potential $V_f(z)$, corrugation function $W(\mathbf{R}, \mathbf{0})$, and particle–substrate coupling $\partial W(\mathbf{R}, \mathbf{0})/\partial \mathbf{u}_i$ are defined as in Ref. 13. $V_f(z)$ and $W(\mathbf{R}, \mathbf{0})$ are obtained from a fit to the MP2 *ab initio* calculation of Ref. 10. The couplings are assumed to have the simple Gaussian form given in Ref. 29:

$$\frac{\partial W(\mathbf{R}, \mathbf{0})}{\partial \mathbf{u}_i} = A e^{-Q_c^2(\mathbf{R}-\mathbf{R}_i)^2/2}, \quad (6)$$

where $\mathbf{R}_i$ is the equilibrium position for the i th surface atom. The values used for A and Q_c are the same as in Ref. 13, where they were fit to DFT calculations. Expanding the lattice displacements $\mathbf{u}_i$ in Eq. (5) in the usual annihilation and creation operators for phonons of wave vector $\mathbf{Q}$, and replacing the discrete sum over i with a continuous integral, valid if the Gaussian is broad with respect to lattice parameter, we obtain

$$V_c(\mathbf{R}, \{\mathbf{u}_i\}) = 2\alpha A \Delta(z) \frac{2\pi}{A_{\text{uc}} N_p^{1/2} Q_c^2} \sum_{\mathbf{Q}} \left(\frac{\hbar}{2M\omega_{\mathbf{Q}}} \right)^{1/2} e^{i\mathbf{Q}\mathbf{R}} \times e^{-\mathbf{Q}^2/2Q_c^2} e_Z(\mathbf{Q})(a_{\mathbf{Q}} + a_{-\mathbf{Q}}^\dagger), \quad (7)$$

where A_{uc} is the unit-cell area, M the lattice atom mass, and N_p is the number of phonons used in the expansion. We rewrite this expression as

$$V_c(\mathbf{R}, \{\mathbf{u}_i\}) = \frac{1}{N_p^{1/2}} \Delta(z) \sum_{\mathbf{Q}} f_{\mathbf{Q}} e^{i\mathbf{Q}\mathbf{R}} (a_{\mathbf{Q}} + a_{-\mathbf{Q}}^\dagger), \quad (8)$$

where

$$f_{\mathbf{Q}} = 2\alpha A \frac{2\pi}{A_{\text{uc}} Q_c^2} \left(\frac{\hbar}{2M\omega_{\mathbf{Q}}} \right)^{1/2} e^{-\mathbf{Q}^2/2Q_c^2} e_Z(\mathbf{Q}). \quad (9)$$

As in Refs. 13 and 21, the phonons included in the calculation are represented by a simple analytical formula for the

frequency $\omega_{\mathbf{Q}}$ and surface projection of polarization vector $e_z(\mathbf{Q})$ given originally in Ref. 23:

$$\omega_{\mathbf{Q}} = \omega_{\max} \sin\left(\frac{\pi Q}{2Q_{\max}}\right), \quad e_z(\mathbf{Q}) = \left(\sin\left(\frac{\pi Q}{2Q_{\max}}\right)\right)^{1/2}. \quad (10)$$

The form chosen for the frequency describes well the low energy acoustic phonon branch, and the one for $e_z(\mathbf{Q})$ which decreases at low wave vector $\mathbf{Q}$ corresponds to a Rayleigh mode which loses its surface character at low Q .³⁰

The formalism presented so far is identical to that used in previous publications.^{13,21,23} We now introduce new ingredients which optimize computational efficiency and open the way to new formalism. One is the basis chosen to represent the system. Instead of using states which represent scattering from a flat surface as was done in Refs. 13 and 21, we introduce here a basis of N_r eigenstates of the Hamiltonian $\mathbf{H}_s$, augmented by a complex absorbing potential $V_{\text{cap}}(z)$ providing an optimal discretization of the continuum along z , following the prescriptions of Ref. 31:

$$(\mathbf{H}_s + V_{\text{cap}}(z)) \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}). \quad (11)$$

These eigenstates thus provide a diagonal representation of the interaction, including corrugation. We will use in Sec. II C the diagonality of the representation of the Hamiltonian to propose a new and efficient wavepacket propagation method. Similarly, in Sec. II E, we will use again this diagonality to define a simple effective Hamiltonian method which improves perturbation theory.

These three-dimensional states $\varphi_i(\mathbf{r})$ are obtained by expansion on a basis of diffraction states describing the motion of the atom parallel to the surface. This motion can be described by plane waves $\langle \mathbf{R}|n, m\rangle = \frac{1}{A_{\text{ac}}^{1/2}} e^{i\mathbf{G}_{\text{mn}}\mathbf{R}}$, where $\mathbf{G}_{\text{mn}}$ belongs to the reciprocal lattice (i.e., m, n integers). We assume throughout the paper perpendicular incidence for the initial state, corresponding to $m = n = 0$. To first-order, the corrugation term $W(\mathbf{R}, \mathbf{0})$ couples this initial state to the six diffraction excited states corresponding to $(m, n) = (\pm 1, 0), (0, \pm 1), (1, 1), (-1, -1)$. These six excited states were used in conjunction with the ground one in the previous works.^{13,21} However, we make use in the present paper of symmetry considerations to reduce the number of necessary diffraction states from 7 to 2, for the case of perpendicular initial incidence. Indeed, the corrugation coupling term belongs to the fully symmetric irreducible representation A_{1g} of the symmetry group of the crystal D_{6h} .³² The initial state $(m, n) = (0, 0)$ also belongs to the A_{1g} irreducible representation and thus only couples to other A_{1g} diffraction states. In the space spanned by the six diffraction excited states, one can form a single A_{1g} state. As a result, we need to retain only the two A_{1g} diffraction states in our treatment, for normal incidence, namely, the initial $(m, n) = (0, 0)$ state and the symmetric linear combination, which we call ground (g) and excited (e) diffraction states in the following.

Creation or annihilation of a phonon with wave vector $\mathbf{Q}$ parallel to the surface induces an opposite change in the momentum of the atom. This could be accounted for exactly by expanding the solutions of Eq. (11) on a basis of modified

plane waves $e^{i(\mathbf{G}_{\text{mn}}+\mathbf{Q})\mathbf{R}}$. This would be extremely time consuming as it would require solving Eq. (11) for each $\mathbf{Q}$. Instead, we use an approximate treatment where the effect of momentum transfer is accounted for by a simple additive factor $\hbar^2 \mathbf{Q}^2/2m$ in Eq. (11) (where m is the H mass), and a simple multiplicative phase factor $e^{\pm i\mathbf{Q}\mathbf{R}}$ in the solution of this equation. This is a good approximation in the present case where the phonon momentum $\mathbf{Q}$ will turn out to be small.

B. Reduced density matrix propagation

We use the reduced density matrix formalism first introduced in Refs. 16–18 and adapted to the present context in Refs. 19 and 20. Assuming that the bath relaxes rapidly or that the bath is only weakly perturbed such that it is never very far from thermal equilibrium, and using the Markov approximation, the equation of evolution for the reduced density matrix (i.e., after tracing over bath states) in the interaction representation is³³

$$\begin{aligned} \frac{d\tilde{\sigma}}{dt} = & -\frac{1}{\hbar^2} \sum_{\mathbf{Q}, \mathbf{Q}'} \int_0^{+\infty} dt'' [S_{\mathbf{Q}}(t), S_{\mathbf{Q}'}(t-t'') \tilde{\sigma}(t)] \\ & \times \langle \mathcal{B}(t'')_{\mathbf{Q}} \mathcal{B}(0)_{\mathbf{Q}'} \rangle \\ & - [S_{\mathbf{Q}}(t), \tilde{\sigma}(t) S_{\mathbf{Q}'}(t-t'')] \langle \mathcal{B}(0)_{\mathbf{Q}} \mathcal{B}(t'')_{\mathbf{Q}'} \rangle, \end{aligned} \quad (12)$$

where

$$\mathcal{B}_{\mathbf{Q}}(t) = e^{(iH_b t)/\hbar} \frac{1}{N_p^{1/2}} f_{\mathbf{Q}}(a_{\mathbf{Q}} + a_{-\mathbf{Q}}^\dagger) e^{-(iH_b t)/\hbar}, \quad (13)$$

$$S_{\mathbf{Q}}(t) = e^{(iH_s t)/\hbar} \Delta(\mathbf{z}) e^{i\mathbf{Q}\mathbf{R}} e^{-(iH_s t)/\hbar}. \quad (14)$$

The brackets in the correlation function $\langle \mathcal{B}(t'')_{\mathbf{Q}} \mathcal{B}(0)_{\mathbf{Q}'} \rangle$ denote a thermal average, and it is easy to show that

$$\begin{aligned} \langle \mathcal{B}(t'')_{\mathbf{Q}} \mathcal{B}(0)_{\mathbf{Q}'} \rangle = & \frac{1}{N_p} f_{\mathbf{Q}} f_{\mathbf{Q}'} \delta_{\mathbf{Q}-\mathbf{Q}'} \\ & \times ((\bar{n}_{\mathbf{Q}} + 1)e^{-i\omega_{\mathbf{Q}} t''} + \bar{n}_{\mathbf{Q}} e^{i\omega_{\mathbf{Q}} t''}), \end{aligned} \quad (15)$$

where $\bar{n}_{\mathbf{Q}} = 1/[e^{(\hbar\omega_{\mathbf{Q}})/kT} - 1]$ (k : Boltzman constant; T : temperature) is the thermal average occupation number.

It is optimal to represent and evolve the RDM using a product basis set, $|\chi_\alpha\rangle|n, m\rangle$, where the $\chi_\alpha(z)$ are the eigenfunctions of the rigid flat-surface Hamiltonian, $K_z + V_f(z) + V_w(z)$, with eigenvalues E_α . As described in the earlier studies,^{13,21} K_z is the z -component of the kinetic energy operator, and V_w is an exponential repulsive wall placed far above the surface. The $|n, m\rangle$ corresponds to the diffraction states, which are eigenfunctions of the parallel component of the kinetic energy operator, with eigenvalues $\kappa_{n,m}$. In this zeroth-order basis, one can derive the following equation of motion:^{19,20}

$$\begin{aligned} \frac{d\sigma_{\alpha p, \beta q}}{dt} = & \frac{i(E_\beta + \kappa_q - E_\alpha - \kappa_p)}{\hbar} \sigma_{\alpha p, \beta q}(t) \\ & - \frac{2i\alpha}{\hbar} \sum_{\gamma, l} [\Delta_{\alpha\gamma} W_{pl} \sigma_{\gamma l, \beta q}(t) - \sigma_{\alpha p, \gamma l}(t) \Delta_{\gamma\beta} W_{lq}] \\ & - \frac{1}{\hbar^2} \sum_{\gamma, \delta} [A_{\alpha\gamma}^- \Delta_{\alpha\gamma} \Delta_{\gamma\delta} \sigma_{\delta p, \beta q}(t) \end{aligned}$$

$$\begin{aligned}
& -A_{\alpha\gamma}^+ \Delta_{\alpha\gamma} \sigma_{\gamma p, \delta q}(t) \Delta_{\delta\beta} - \Delta_{\alpha\gamma} \sigma_{\gamma p, \delta q}(t) A_{\delta\beta}^- \Delta_{\delta\beta} \\
& + \sigma_{\alpha p, \gamma q}(t) \Delta_{\gamma\delta} A_{\delta\beta}^+ \Delta_{\delta\beta}
\end{aligned} \quad (16)$$

which is used as a short time propagator for the RDM (Refs. 13, 19–21). We stress that while we have assumed that the atom-bath interaction is weak and all instantaneous interactions are “single-phonon,” the atom is in continuous contact with the bath while it is on or near the surface, and it can exchange many quanta of energy with the bath over long times, eventually relaxing or desorbing. In Eq. (16), $\sigma_{\alpha p, \beta j}(t) = \langle \chi_\alpha | \langle p | \sigma | q \rangle | \chi_\beta \rangle$, $\Delta_{\alpha\beta} = \langle \chi_\alpha | \Delta | \chi_\beta \rangle$, and $W_{pq} = \langle i | W | q \rangle$. The Greek subscripts label the basis χ_α . The subscripts p , q , and l label the diffraction basis, where each corresponds to a pair of numbers (n, m) . We have $A_{\alpha\gamma}^+ = A_{\gamma\alpha}^+$, where $A_{\alpha\beta}^+ = \pi f_{\mathbf{Q}}^2 \eta(\omega_{\mathbf{Q}}) (\bar{n}_{\mathbf{Q}} + 1)$, where $\omega_{\mathbf{Q}} = (E_\alpha - E_\beta)/\hbar$ if $E_\alpha < E_\beta$ and $A_{\alpha\beta}^+ = \pi f_{\mathbf{Q}}^2 \eta(\omega_{\mathbf{Q}}) (\bar{n}_{\mathbf{Q}})$, where $\omega_{\mathbf{Q}} = (E_\beta - E_\alpha)/\hbar$ if $E_\alpha > E_\beta$. $\eta(\omega)$ is the phonon density of states normalized to 1.

For weak corrugation, the zeroth-order states defined by our product basis are similar to the true three-dimensional rigid-surface eigenstates defined by Eq. (11). In earlier studies using this RDM formalism, probabilities and transition rates were defined in terms of these zeroth-order product states.^{13,21} This led to some errors, as well as Rabi-type oscillations in the probabilities, because the corresponding states are no more eigenstates of $\mathbf{H}_s$ when corrugation is included. In this study, we retain the use of this zeroth-order product basis only for the evolution of the RDM. As discussed in earlier work,^{13,21} this choice for a basis, and the form of the corrugation and phonon couplings, allows for certain factorizations that significantly increase numerical efficiency. However, we have diagonalized the full three-dimensional rigid-surface Hamiltonian using our product basis, and use this to transform between our working product basis and the full three-dimensional (rigid surface) eigenstates defined by Eq. (11). Thus, all probabilities and transitions reported in this work correspond to the correct three-dimensional eigenstates.

C. Close coupling wavepacket (CCWP)

We follow the formalism originally given in Refs. 22 and 23, but adapt it to the resonant basis given by Eq. (11). The wavepacket is expanded onto bath states $|\{n\}_{\lambda\mathbf{Q}}\rangle$ and basis functions $\varphi_i(\mathbf{r})$ already defined in Eq. (11):

$$\psi(\mathbf{r}, t) = \sum_{i=1-N_r, \lambda=0, \pm 1, \mathbf{Q}} c_i^{\lambda\mathbf{Q}}(t) e^{-i\lambda\mathbf{Q}\mathbf{R}} \varphi_i(\mathbf{r}) |\{n\}_{\lambda\mathbf{Q}}\rangle. \quad (17)$$

The bath is characterized by a set of occupation numbers $\{n\}$ giving the excitation level of the different phonon states $\mathbf{Q}$. The initial state corresponds to $\lambda = 0$. By interaction with the hydrogen atom, the bath can de-excite by annihilating ($\lambda = -1$) a phonon with momentum $\mathbf{Q}$ or excite by creating ($\lambda = +1$) one. The subscript $\lambda\mathbf{Q}$ in the bath state representation $|\{n\}_{\lambda\mathbf{Q}}\rangle$ therefore indicates differences with respect to the initial bath state. The bath states considered in Eq. (17) are assumed to be normalized. Notice also that the expansion of the wavefunction is truncated to bath states different from the initial one by a single phonon. Therefore, processes involving

simultaneous or sequential creation or annihilation of several phonons are not described by this formalism.

The coefficients of the expansion are solutions of a set of $(2N_p + 1)N_r$ coupled equations:

$$\begin{aligned}
i\hbar \frac{dc_i^{\lambda\mathbf{Q}}(t)}{dt} = & \left(\epsilon_i + \frac{\hbar^2 \lambda^2 Q^2}{2m} + \lambda \hbar \omega_{\mathbf{Q}} \right) c_i^{\lambda\mathbf{Q}}(t) \\
& + \sum_{i', \lambda', \mathbf{Q}'} V_c^{\lambda\mathbf{Q}i' \lambda' \mathbf{Q}'} c_{i'}^{\lambda' \mathbf{Q}'}(t).
\end{aligned} \quad (18)$$

From Eq. (8), it is clear that the coupling matrix can be nonzero only when $\lambda = 0$ or $\lambda' = 0$. It is complex symmetric and its elements simplify into

$$V_c^{\lambda=0 \mathbf{Q}i' \lambda'=1 \mathbf{Q}'} = \frac{(\bar{n}_{\mathbf{Q}'} + 1)^{1/2}}{N_p^{1/2}} f_{\mathbf{Q}'}(\varphi_i(\mathbf{r}) | \Delta(z) | \varphi_{i'}(\mathbf{r})), \quad (19)$$

$$V_c^{\lambda=0 \mathbf{Q}i' \lambda'=-1 \mathbf{Q}'} = \frac{\bar{n}_{\mathbf{Q}'}}{N_p^{1/2}} f_{\mathbf{Q}'}(\varphi_i(\mathbf{r}) | \Delta(z) | \varphi_{i'}(\mathbf{r})). \quad (20)$$

These equations are obtained from Eq. (17) after thermal averaging over the different possible occupation numbers, leading the average $\bar{n}_{\mathbf{Q}}$ at temperature T .

The choice of embedding the optical potential in the resonance basis [Eq. (11)] produces a complex symmetric instead of hermitian coupling matrix. Many wavepacket propagators (Lanczos, Chebychev, Split etc.) may have stability problems in such a context. We use instead the Crank–Nicholson propagator³⁴ which requires solving a set of $(2N_p + 1)N_r$ linear equations at each time step. This is time consuming in the general case but we show in the Appendix that it is very efficient and robust in the present context resulting from the particular choice of the resonance basis defined by Eq. (11). The populations in the various states are given by $P_{\lambda\mathbf{Q}i}(t) = |c_i^{\lambda\mathbf{Q}}(t)|^2$. These quantities can be summed over phonon or resonance states according to the desired physical quantities. Their values at long times for negative energy states provide stuck populations.

D. Perturbation theory (PT)

We now assume that the dynamics of the H atom in the $\lambda = 0$ subspace is unchanged by energy exchange with the substrate. Since we know the eigenvalues of the system in this subspace, time evolution is given straightforwardly by

$$c_i^{\lambda=0}(t) = e^{-i\epsilon_i t/\hbar} c_i^{\lambda=0}(0), \quad (21)$$

(notice that the $\mathbf{Q}$ superscript has been removed because it has no use in the subspace $\lambda = 0$).

Equation (18) for $\lambda = \pm 1$ can now be integrated analytically because the right-hand side which corresponds to $\lambda' = 0$ is fully known, thanks to Eq. (21):

$$\begin{aligned}
c_i^{\lambda\mathbf{Q}}(t) &= \exp \left[-i(\epsilon_i + (\hbar^2 Q^2)/2m + \lambda \hbar \omega_{\mathbf{Q}})t/\hbar \right] \sum_{i', \mathbf{Q}'} V_c^{\lambda\mathbf{Q}i' \lambda'=0 \mathbf{Q}'} \\
&\times \frac{1 - \exp[i(\epsilon_{i'} + (\hbar^2 Q'^2)/2m + \lambda \hbar \omega_{\mathbf{Q}'} - \epsilon_i')t/\hbar]}{\epsilon_i + \frac{\hbar^2 Q^2}{2m} + \lambda \hbar \omega_{\mathbf{Q}} - \epsilon_i'} c_{i'}^{\lambda'=0}(0),
\end{aligned} \quad (22)$$

from which the different trapped and stuck populations can be extracted easily.

E. Effective Hamiltonian method (EH)

Perturbation theory described above does not allow to take into account the feedback of the dynamics in the $\lambda = \pm 1$ subspace onto the $\lambda = 0$ one. Effective Hamiltonian theory^{28,35} provides some correction to this shortcoming. This effective Hamiltonian is obtained by the same partition of the basis used to describe the dynamics as the one described in the Appendix. The restriction of the resolvent of the system (a function of complex variable ζ) in the $\lambda = 0$ subspace can be written in terms of an effective Hamiltonian defined as

$$\mathbf{H}^{\text{eff}}(\zeta) = H_{00} + H_{0\pm 1}(\zeta - H_{\pm 1\pm 1})^{-1}H_{\pm 10}. \quad (23)$$

The second term of this equation provides a correction to H_{00} used in perturbation theory which describes coupling between both subspaces of the partition. Manipulation of the effective Hamiltonian is not easy in practice as it involves integration in the complex plane of this complicated operator. A drastic simplification is obtained by approximating the effective Hamiltonian by its value at some value of ζ_0 . In the following, for the case of an incoming wavepacket on the surface, we assume that this value is the average energy of the wavepacket. Diagonalization of $\mathbf{H}^{\text{eff}}(\zeta_0)$ provides modified resonances $\varphi_i^{\text{eff}}(\mathbf{r})$, which include some effect of the coupling between $\lambda = 0$ and $\lambda = \pm 1$ subspaces. Dynamics in both subspaces is still given by Eqs. (21) and (22), where the $c_i^{\lambda} Q(t)$ coefficients refer to the expansion of the wavefunction on the new modified resonances. The eigen-energies ϵ_i and coupling elements $V_c^{\lambda=0Q_i \lambda' Q' i'}$ are also defined with respect to this new basis.

F. Calculation parameters

The lattice parameter is $a = 2.46 \text{ \AA}$. The phonons are described by Eq. (10) with $\omega_{\text{max}} = 524 \text{ cm}^{-1}$ and $Q_{\text{max}} = 4\pi/3a$. The 1st Brillouin zone is discretized to create a set of 251 phonons. The motion of the H atom is described using a grid of 300 points in a box extending from 1 to 150 a.u. A set of 200 resonances [Eq. (11)] are used to describe the system. For all calculations except the RDM, they are obtained using the optimized absorbing potential of Ref. 31, an order 3 polynomial corresponding to an error 10^{-4} , and an energy band where the lowest to highest energy ratio is 1/30. For the RDM evolution, no absorbing potential was used as it leads to numerical divergence of the short time propagator. The 300 points grid used here is large enough to avoid problems with reflection from the boundary at large z .

The initial state of the system is represented by a Gaussian wavepacket centered at 50 a.u. from the surface with a spatial width giving an energy uncertainty of 0.9 meV for all incident energies. The time step used for the Crank–Nicholson propagator was 7.25 fs. The ζ_0 chosen for the effective Hamiltonian formalism is the central energy of the Gaussian wavepacket.

TABLE I. Resonant state energies and their lifetimes obtained from solution of Eq. (11). Energies of approximate separable states are also shown. These states are obtained by neglecting the coupling between the diffraction states and they can be labeled by quantum numbers which are approximate for the resonant states. The first one v describes vibration of the H atom with respect to the surface, the second one corresponds to the diffraction state g or e .

Resonant state energy (meV)	Lifetime (ps)	Separable state energy (meV)	Quantum numbers
−25.22	∞	−24.96	(0,g)
−11.21	∞	−10.58	(1,g)
−7.67	∞	−8.07	(0,e)
−2.92	∞	−2.90	(2,g)
−0.43	∞	−0.41	(3,g)
−0.01	∞	−0.01	(4,g)
6.88	0.94	6.81	(1,e)
15.03	1.89	15.00	(2,e)
17.82	7.94	17.81	(3,e)
18.29	93.94	18.29	(4,e)

The computing times on a single Xeon processor per energy are typically of the order of a few seconds for the PT and EH methods, and a few minutes for RDM and CCWP. Alternatively, one could use a single broad wavepacket instead of several narrow ones centered on different energies to obtain results in a given energy band. One advantage of the present method with several wavepackets is that it provides the time dependance of the trapping probabilities for narrow band excitation, from which physically meaningful information can be extracted.

III. RESULTS

A. Sticking

Table I shows the energies and lifetimes of a few resonant states obtained by solving Eq. (11). As expected,^{13,21} the lowest energy states correspond to states of the H atom bound in the physisorption well, but higher energy states are unbound and have finite lifetimes. These resonances can be approximated by bound states obtained by diagonalizing the static surface Hamiltonian for the case where coupling between the g (ground) and e (excited) diffraction states is neglected. These are equivalent to the zeroth-order states used in the RDM propagation. Their energies and corresponding quantum numbers are shown in Table I. The first one is the vibrational quantum number v describing the motion of the H atom perpendicular to the surface, and the second the diffraction label g or e for the motion parallel to the surface.

Figure 1 shows the probabilities for sticking in various bound states as a function of time for an initial collision energy of 7 meV and for surface temperatures of 10 and 300 K. We use the usual convention that a particle bound to the surface in the z -direction is trapped if it has a total energy that is positive, and it is stuck if its total energy is negative. Our zero of energy here corresponds to an atom with zero kinetic energy far above the surface. We focus on the populations of the

FIG. 1. Stuck state-resolved populations as a function of time at 10 K (upper frame) and 300 K (lower frame). The initial state corresponds to an hydrogen atom described by a Gaussian wavepacket centered at $z = 50$ a.u. and $E = 7$ meV average energy. The energy uncertainty is 0.9 meV. The labels of the populations are the quantum numbers of the states considered : $v = 0, 1$, or 2 describes the motion of the stuck H-atom perpendicular to the surface, and g/e refers to the ground or excited mode parallel to the surface. Lines: CCWP results, line-points: RDM results.

four lowest energy bound states, which are bound by nearly 3 meV or more. The primary mechanism for sticking into these states is the excitation of a single phonon with an energy equal to the difference between the incident collision energy and the energy of the corresponding bound state. Sticking is more efficient at 300 K than at 10 K because the phonon occupation numbers, and thus the thermally averaged coupling [see Eq. (19)], increase with temperature. Both the CCWP and RDM formulations capture the essential features of the sticking process, and there are only minor differences between the results. In the CCWP formalism, the trapped populations all increase with time, becoming constant once the incident wavepacket scatters away from the surface and the coupling matrix elements go to zero. For the RDM case, desorption can cause the populations to decrease after reaching a maximum, especially when the surface temperature is high. Indeed, in our CCWP formalism, the wavepacket is expanded on a basis including only creation or annihilation of a single phonon with respect to the initial state. If the initial state is the incoming hydrogen, then only sticking to the surface can be described within this formalism, as subsequent desorption modeling would require extension of the space on which the wavefunction is expanded, which is out of reach of present computer capabilities. However, we will show later in this paper that desorption can be taken into account with the CCWP

approach if a stuck hydrogen instead of an incoming one is considered as the initial state. By contrast, the RDM formalism is capable of describing continuous interactions between the system and the bath. Thus, a trapped or stuck atom can continue to lose energy to the bath, relaxing to lower energy bound states, or it can gain energy from the bath and desorb. At 10 K, the postcollision (after 5 ps or so) RDM probabilities are relatively constant in time, only relaxing to an equilibrium distribution at time scales much longer than that shown. At 10 K, desorption time scales are effectively infinite, and the postcollision sticking probability at 10 K corresponds to the measured sticking probability. At 300 K, this energy exchange is more rapid. Following the initial collision, we see both a relaxation from $v = 1$ to $v = 0$ of the ground diffraction state, as well as desorption from the $v = 0$ excited diffraction state. On experimental time scales, for 300 K, all of the sticking probabilities for the RDM case will go to zero, and thus there is no measurable sticking. For the present case, the postcollision CCWP and RDM results are close even at 300 K. This means that the single phonon approximation of the CCWP case is reasonable, and that desorption is a slower process which plays only a minor role on the time scale considered here.

For collision energies near 7 meV, there is a second trapping/sticking mechanism. For energies close to those of the resonances (v, e) associated with the excited diffraction state, the H atom can become temporarily trapped on the surface. Physically, the atom transfers some of its energy from motion perpendicular to the surface into motion parallel to it, ending up in one of the bound states, though the total energy of the particle is unchanged, and still positive. This mechanism is usually referred to as diffraction mediated selective adsorption (DMSA) (Ref. 36). In our case, this process can be further enhanced by the absorption or excitation of a phonon, broadening the resonance. For the 7 meV energy considered here, the resonant state at play is the ($v = 1, e$). As explained in Ref. 13, the incident atoms can become trapped in the ($v = 1, e$) state, and while trapped on the surface and in contact with the bath, excite phonons and relax into the ($v = 0, e$) state, becoming truly stuck. This is why the ($v = 0, e$) stuck population is significantly larger than the (v, g) ones.

Figure 2 shows the postcollision probabilities for sticking in the same four final states as a function of collision energy for the same surface temperatures as in Fig. 1. As already seen in Fig. 1, sticking increases with temperature. The importance of DMSA in enhancing trapping and sticking is clearly visible in Fig. 2. Three peaks, related to the ($v = 1 - 3, e$) resonances (see Table I) at 7, 15, and 18 meV, are clearly visible in the ($v = 0, e$) final population. Again, there is significant trapping in these DMSA resonances, followed by relaxation to the negative energy ($v = 0, e$) state via phonon excitation. Away from these resonances, sticking in this final state is almost zero. By contrast, sticking probabilities in the other states ($v = 0 - 2, g$) is significant for all energies and has a weaker dependance on energy. This is the fingerprint of a direct sticking process not mediated by resonances. Close to the energies of the ($v = 1 - 3, e$) resonances, the interference between this direct process and the DMSA one produces different kinds of line shapes for the stuck

FIG. 2. Individual sticking probabilities at 10 and 300 K as a function of the collision energy obtained from CCWP. The initial state is a wavepacket centered at $z = 50$ a.u. with a 0.9 meV energy uncertainty. The quantum numbers of the populated states are defined in the caption of Fig. 1.

populations: absorption ($\nu = 1, g$), emission ($\nu = 0, g$), and intermediate ($\nu = 1, g$). This is an illustration of the standard theory of resonances, as described for instance in Ref. 37 (Section 4.3). Figure 3 shows total postcollision sticking probabilities, summed over all final bound states. The effect of DMSA is emphasized by the comparison with the flat-surface calculation, where the e diffraction channel is not included. If the DMSA contributions are omitted from the corrugated surface result, the resulting sticking probability is close to the flat-surface one. The direct mechanism mentioned in the preceding paragraph which interferes with the resonant one is thus the flat-surface contribution.

Figure 3 also allows us to compare the relative accuracy of the different RDM, CCWP, EH, and PT methods. For the RDM case, we use the maximum postcollision values. All four methods give results that are in good agreement with each other. At higher temperature, PT overestimates the sticking probability. Indeed, as phonon creation and annihilation occurs, the amplitude of the initial state should decrease accordingly. This decrease would in turn further decrease phonon-inelastic events at later times. As a result, PT is expected to overestimate trapping and sticking probabilities. This is corrected by the EH formalism, which provides lower sticking populations because the initial state population is lowered as phonon-inelastic scattering occurs. However, it turns out that for specific energies, the EH results are not correct. This is a consequence of the fixed energy approximation used in our treatment (see Sec. II E). Finally, the CCWP

FIG. 3. Total sticking probabilities at 10 and 300 K as a function of collision energy. Different models are compared: connected filled circles: RDM; blue continuous lines: CCWP; empty circles: EH; red lines: PT. At 10 K, EH is not shown because it is almost indistinguishable from PT results. Also, at 10 K, RDM (connected filled circles) and CCWP results (plain line) for a flat surface (no diffraction) are also shown.

and RDM results are very similar. At 10 K, the RDM sticking probabilities are larger than for the CCWP approach, particularly near the resonances. This is likely due to the existence of additional (sequential) multiphonon processes in the RDM treatment that relax atoms trapped in the DMSA resonances. In fact, in Fig. 1, the ($\nu = 0, e$) population at 10 K is significantly larger than for the CCWP case. There is also some additional scattering into the $\nu = 0$ and $\nu = 1$ bound states of the ground diffraction channel, possibly due to small multiphonon contributions. At 300 K, desorption processes become important for the RDM case. Thus, some of the stuck atoms can begin to desorb immediately after they stick. As a result, the maximum post-collision trapping probability is a bit smaller than it would be in the absence of desorption. Because of this, the CCWP and RDM results are in even better agreement at 300 K.

B. Desorption

The results presented in Sec. III A described sticking weakly perturbed by desorption (for the RDM case), and were computed for an initial state corresponding to an H atom approaching the surface. We now specifically consider the case of desorption, where the initial state of the system corresponds to one of the bound state solutions of Eq. (11). This

allows us to obtain information on the desorption process, even from methods such as CCWP which were not able to take this process into account given the initial state of Sec. III A and the basis set used.

Multiphonon processes can be important in desorption, and the RDM approach should describe the desorption of physisorbed H from graphite very well, given the validity of the weak coupling assumption for this system. However, the CCWP approach has to be modified before being compared to the RDM results. An important deficiency of the CCWP approach is related to the fact that it allows significant low frequency phonon excitation and absorption without changing the particle state. Such transitions are not treated properly in CCWP because only a single excitation or absorption can occur. The initial state population is depleted unphysically. Let us call $P_{i_0,\lambda_0}^{i,\lambda}(t)$ the population of a given state (i, λ) for a desorption process starting from the state (i_0, λ_0) . The index i represents for instance the approximate quantum numbers v and g/e . The phonon state $\lambda = 0, \pm$ has been defined in Sec. II C (we use $\pm$ as a short hand notation for ± 1).

Let us assume, we start from the phonon state $\lambda_0 = 0$. In CCWP, a population $P_{i_0,0}^{i_0,\pm}(t)$ associated with the same particle state as the initial one but different phonon states builds up. This induces a nonphysical decrease of the initial population $P_{i_0,0}^{i_0,0}(t)$. The populations of $(i_0, \pm)$ cannot decay back to the initial state because this would require a second phonon. Considering a sum over phonon final states, $P_{i_0,0}^{i_0}(t) = \sum_{\lambda} P_{i_0,0}^{i_0,\lambda}(t)$ does not solve the problem. $P_{i_0,0}^{i_0}(t)$ obtained from CCWP is larger than the correct RDM result. Indeed, the contributions $P_{i_0,0}^{i_0,\pm}(t)$ to the sum are larger than they should be, as they cannot be depleted by transitions to other particle states, due to the unavailability of extra phonon terms in the CCWP expansion.

However, a correction to the CCWP populations providing a better agreement with the RDM results is possible. The initial state population has an approximate exponential decay: $P_{i_0,0}^{i_0,0}(t) = e^{-K_{i_0,0}t}$. All final possible states contribute to $K_{i_0,0}$, including the states $(i_0, \pm)$. A correction can be applied to CCWP results which provides much better agreement to RDM ones. The procedure goes as follows:

- (1) Fit the decay of $P_{i_0,0}^{i_0,0}(t)$ to an exponential law. This provides the total decay rate $K_{i_0,0}$.
- (2) Fit the increase of the populations $P_{i_0,0}^{i,\pm}(t)$: $P_{i_0,0}^{i,\pm}(t) = p_{i_0,0}^{i,\pm}(1 - e^{-K_{i_0,0}t})$. This allows one to define a partial decay rate: $K_{i_0,0}^{i,\pm} = p_{i_0,0}^{i,\pm}K_{i_0,0}$.
- (3) Define a corrected decay rate, which is obtained by summing over all final states except the one which corresponds to the same particle state: $\bar{K}_{i_0,0} = \sum_{i \neq i_0, \lambda} K_{i_0,0}^{i,\lambda} = K_{i_0,0} - K_{i_0,0}^{i_0,+} - K_{i_0,0}^{i_0,-}$.
- (4) Define corrected CCWP populations: $\bar{P}_{i_0,0}^{i_0,0}(t) = e^{-\bar{K}_{i_0,0}t}$ and $\bar{P}_{i_0,0}^{i,\pm}(t) = p_{i_0,0}^{i,\pm} \frac{K_{i_0,0}}{\bar{K}_{i_0,0}} (1 - e^{-\bar{K}_{i_0,0}t})$.

Figure 4 compares the RDM and CCWP results for the population remaining in the initial bound state $\bar{P}_{i_0,0}^{i_0,0}(t)$ and the total stuck population $\sum_{i,\lambda} \bar{P}_{i_0,0}^{i,\lambda}(t)$ (the sum over i is over the bound states), after application of this correction. The agreement between the corrected CCWP and the RDM is ex-

FIG. 4. Desorption at 300 K. Upper frame: population remaining in the initial state as a function of time. Each line color corresponds to a different initial stuck state. Lower frame: Total stuck population, defined as the sum over the populations of all the bound states of the system ($v = 0 - 4, g + v = 0, e$), as a function of time. Each line color corresponds to a different initial stuck state. Lines: corrected CCWP results, see text for the correction procedure. Line-points: RDM results.

cellent for the initial state population over a time interval of the order of 10 ps. The decay rate is close to exponential and the corresponding time constants are given in Table II. All four states decay with a time constant of the order of 20 ps, except for the $(1, g)$ state, which decays faster with a time constant of the order of 10 ps.

However, agreement is not so good for the total stuck populations (Fig. 4, bottom frame). Multiphonon processes play a significant role in this case. Desorption may be achieved only after several phonon absorption steps, and such a multistep process cannot be accounted for by CCWP. As a result, desorption is underestimated by CCWP. The decay

TABLE II. Time constants for exponential decay of the initial state (from modified CCWP results) and total trapped populations (from RDM results). Four different initial states are considered, labeled by the approximate quantum numbers v and g/e describing motion perpendicular and parallel to the surface, respectively. Surface temperature is 300 K.

Initial state	Initial population decay (ps)	Stuck population decay (ps)
(0,g)	21	48
(1,g)	10	26
(0,e)	20	22
(2,g)	19	37

FIG. 5. Individual populations in different stuck states, for $v = 0 - 1, g$ initial states. Surface temperature is 300 K. Lines: corrected CCWP results, line-points: RDM results.

of the total trapped probability is close to exponential for the RDM case, corresponding to a constant desorption rate. Corresponding decay times are given in Table II. Typically, the decay rate of the total trapped population is half that of the initial population, with the exception of the $(0, e)$ initial state for which initial state decay and total population decay have similar time constants. This is due to the fact that in the general case, there is a competition between transitions to other bound states and transitions which lead to desorption. For the $(0, e)$ initial state, however, direct desorption is more efficient than transitions to other bound states.

Figures 5 and 6 show individual populations $P_{i_0,0}^i(t)$ for the modified CCWP case compared with the RDM results. At short times, agreement is good, but at longer times, multiphonon processes play a significant role. CCWP populations which cannot decrease by any transition, which would require additional phonons, are therefore larger than the RDM ones. The dominant transitions are between states in the same diffraction channel (g or e). Transition rates for each transition could be obtained by exponential fits to these CCWP populations. A master equation could then be written in terms of these transition rates as done for instance in Ref. 26. It is a kinetic model corresponding to a set of first-order coupled differential equations on the populations. Solution of this system would provide populations in better agreement with RDM ones, but this goes beyond the scope of the present paper.

FIG. 6. Same as Fig. 5 for $v = 0, e$ and $v = 2, g$ initial states.

IV. CONCLUSION

We have presented a quantum mechanical study of the physisorption of hydrogen on graphite. We considered both sticking and desorption processes. We compared four methods: perturbation and effective Hamiltonian theories, close coupling wavepacket, and reduced density matrix approaches. For sticking, we showed that the four methods give results in good agreement, even at a 300 K surface temperature. We highlighted the effect of diffraction mediated resonances in the enhancement of trapping and sticking probabilities. Typical values for sticking probabilities are a few percent, larger at the DMSA resonance energies, and they increase with surface temperature. For desorption, we compared the ability of CCWP and RDM to provide desorption rates. We showed that both CCWP and RDM are capable of describing correctly the decay of the initial state, but only the RDM is capable of describing the decay of the total trapped population. The desorption time constants are very large at 10 K and in the range 20–50 ps for a surface temperature of 300 K. A natural continuation of this work is the study of chemisorption. This case corresponds to a stronger atom-surface coupling, and it is likely that perturbation methods will not be accurate and that many phonon processes will play a more important role.

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APPENDIX

Rewriting the set of equations (18) in matrix form, and defining a vector $\mathbf{c}(t)$ from the $(2N_p + 1)N_r$ coefficients $c_i^{\lambda Q}(t)$, we have $i\hbar d\mathbf{c}(t)/dt = (\mathbf{H}_0 + \mathbf{V}_c)\mathbf{c}(t)$. $\mathbf{H}_0$ is a diagonal matrix and $\mathbf{V}_c$ a sparse matrix with nonzero elements in the $N_r \times (2N_p)N_r$ blocks connecting the N_r : $\lambda = 0$ states with the $(2N_p)N_r$: $\lambda = \pm 1$ ones. The Crank–Nicholson method relies on a second-order approximation of the short-time step dt evolution operator: $e^{-i(\mathbf{H}_0 + \mathbf{V}_c)dt/\hbar} \approx (1 - i\mathbf{H}_0 dt/2 - i\mathbf{V}_c dt/2)(1 + i\mathbf{H}_0 dt/2 + i\mathbf{V}_c dt/2)^{-1}$. The set of linear equations $\mathbf{A}\mathbf{x} = \mathbf{b}$ to be solved at each time step involves the matrix $\mathbf{A} = 1 + i\mathbf{H}_0 dt/2 + i\mathbf{V}_c dt/2$ and vectors of length $(2N_p + 1)N_r$: $\mathbf{x}$ and $\mathbf{b}$. By separating in the $(2N_p + 1)N_r$ basis states the N_r which correspond to $\lambda = 0$ from the $2N_p N_r$ ones corresponding to $\lambda = \pm 1$, we partition this matrix in blocks:

$$\mathbf{A} = \begin{pmatrix} A_{00} & A_{0\pm 1} \\ A_{0\pm 1}^t & A_{\pm 1\pm 1} \end{pmatrix}, \quad (24)$$

where the lower left block of the matrix is the transpose of the opposite one. Similarly, we can partition vectors $\mathbf{x}$ and $\mathbf{b}$ in components x_0 (b_0) and $x_{\pm 1}$ ($b_{\pm 1}$) of lengths N_r and $2N_p N_r$. A_{00} and $A_{\pm 1, \pm 1}$ are square matrices of sizes N_r and $2N_p N_r$, respectively. They are also diagonal and correspond to the restrictions of $1 + i\mathbf{H}_0 dt/2$ to the $\lambda = 0$ and $\lambda = \pm 1$ subspaces, respectively. $A_{0\pm 1}$ is a $N_r \times (2N_p)N_r$ rectangular matrix corresponding to the nonzero elements of $\mathbf{V}_c$. Standard partitioning technique then provides

$$(A_{00} - A_{0\pm 1} A_{\pm 1\pm 1}^{-1} A_{0\pm 1}^t) x_0 = (b_0 - A_{0\pm 1} A_{\pm 1\pm 1}^{-1} b_{\pm 1}). \quad (25)$$

Writing this system of equations involves inversion of $A_{\pm 1\pm 1}$ block, but this is a straightforward task because this matrix is diagonal. This system can be easily solved because it involves N_r equations only. Once x_0 is known, $x_{\pm 1}$ is obtained from

$$x_{\pm 1} = A_{\pm 1\pm 1}^{-1} (b_{\pm 1} - A_{0\pm 1}^t x_0). \quad (26)$$

Forming the right-hand side of Eq. (25) requires operations of the order of $N_p N_r^2$ [multiplication of a vector of length $2N_p N_r$ by a $N_r \times (2N_p N_r)$ matrix]. Forming the left-hand side of Eq. (25) requires more operations, $N_r^3 N_p$, but

this step needs to be performed only once at the first time step. Solving Eq. (25) requires operations of the order of N_r^2 . Then obtaining x_1 from Eq. (26) requires $N_p N_r^2$ operations. The total number of operations at each time step is thus of the order of $N_p N_r^2$, and this is also the number of operations needed to multiply the sparse matrix $\mathbf{A}$ with a vector. As a result, the present algorithm which involves linear system solving is as efficient as wavepacket propagation techniques based solely on matrix multiplications (Chebychev, Lanczos etc.).

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