

β -decay spectrum of tritiated graphene: Combining nuclear quantum mechanics with density functional theory

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We present the results of a multimethodological study aimed at investigating the interaction between graphene and tritium during its β -decay to helium, under different levels of loading and geometrical configurations. We combine density-functional theory (DFT) to evaluate the interaction potentials, with calculations of the decay rate, in order to study the consequences that the presence of the substrate has on the β -decay spectrum of tritium. We determine the shape of the event rate, accounting for the effects of (part of) the corresponding condensed-matter degrees of freedom. In the context of future neutrino experiments, our results provide important information aimed at the optimization of hosting material. Furthermore, our work outlines a novel theoretical and computational scheme to account for the different timescales involved in the process and to address a question at the boundary between high- and low-energy physics. This requires nonconventional declinations of DFT combined with full quantum treatments of the nuclear configuration involved in the decay process. Our results pave the way for future studies aimed at determining the physics reach of upcoming neutrino mass experiments.

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I. INTRODUCTION

Of all the known fundamental particles, neutrinos are arguably the most elusive ones, mostly because, aside from gravity, they couple to the rest of ordinary matter only via weak interactions, which, at low energies, are extremely feeble. Moreover, while within the renormalizable part of the standard model they are exactly massless, the experimental observation of the oscillations between their three flavors (i.e., electronic, muonic, and tauonic) indeed implies that they do carry mass [1–6]. These masses, however, are still unknown, both in their absolute value (i.e., the mass of the lightest neutrino) and in their ordering (i.e., whether the lightest neutrino is mostly within the electronic or tauonic family).

A possible way to measure these properties is by looking at the spectrum of the electrons emitted by β -decay processes of unstable nuclei. Among them, a notable instance is the decay of tritium (i.e., ${}^3\text{He}$, hereafter also noted as T),

$$\text{T} \rightarrow {}^3\text{He} + e + \bar{\nu}_e, \quad (1)$$

which produces an electron, an antineutrino, and a helium nucleus. The shape of the spectrum for values of the electron's energy close to the maximum allowed one—the so-called end point—is the most sensitive to the neutrino masses, which can then, in principle, be inferred from its precise measurement. The tritium lifetime of about 12 years, and its relatively low energy end point of 18.6 keV, makes it particularly amenable to this aim, motivating a series of tritium β -decay experiments [see, e.g., Refs. 7–10]. The current best laboratory bound on the neutrino (effective) mass has been set by the KATRIN experiment, which obtained $m_\nu < 0.45$ eV, using gaseous molecular tritium [11–13].

Other proposed projects like PTOLEMY [14–18] or Project8 [19,20] aim at improving this bound by employing tritium in different forms. In particular, PTOLEMY plans to distribute it on a solid substrate, with the advantage of achieving extremely high concentrations, thus maximizing the number of observed events. Albeit with additional difficulties, a similar strategy could also allow the detection of the elusive cosmic neutrino background, via the neutrino capture process

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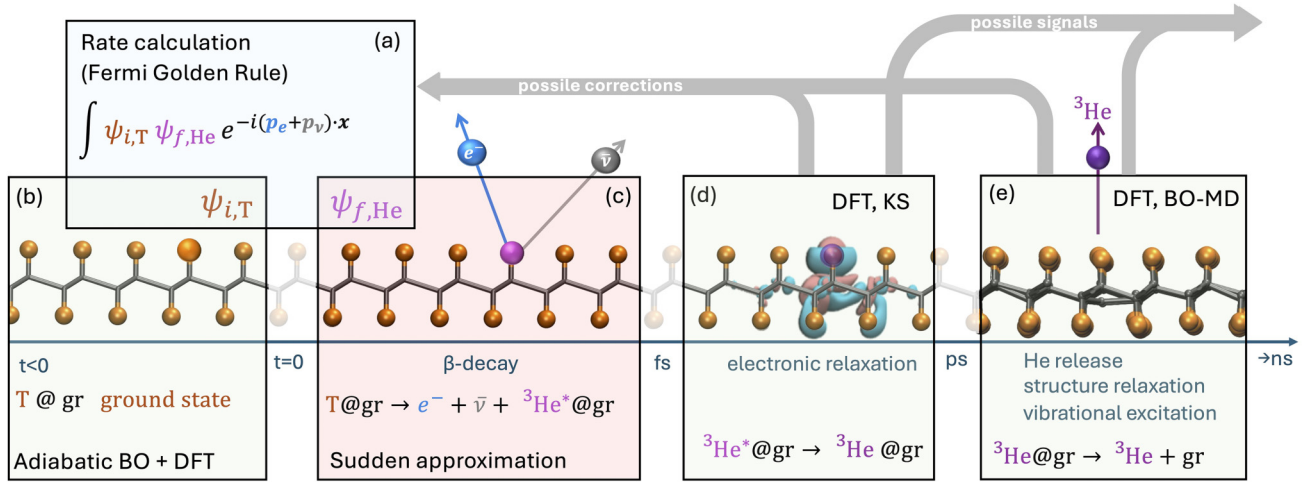


FIG. 1. Scheme of the theoretical framework and calculations performed in this work. (a) Calculation of the matrix element between initial and final states to evaluate the decay rate spectrum. (b) DFT calculation of the tritium potential on graphene in the initial ground state. (c) Sudden approximation for the calculation of the potential felt by helium just after the decay. (d) DFT calculation of the electronic relaxation via the Kohn-Sham (KS) scheme. (e) Born-Oppenheimer dynamics (BO-MD) of the system after the electronic relaxation. Shorthand notations: T is tritium ${}^3H$, the asterisk * indicates an electronically excited state, and the suffix @gr indicates the bond to graphene.

[15,21,22], i.e.,

$$\nu_e + T \rightarrow {}^3He + e. \quad (2)$$

The substrate of choice has been identified as graphene, whose capability of covalently binding hydrogen [23] in almost 1:1 stoichiometry with carbon was recently demonstrated for nanoporous samples, displaying up to 90% loading [24]. Moreover, its low-dimensional nature allows us to minimize uncontrolled energy losses for the outgoing electron [25]. Thanks to this, the project has the potential of reaching an unprecedented sensitivity to the effective neutrino mass (see, e.g., Ref. [15] for an estimate).

Hydrogen (and tritium) chemisorption alters the structural, chemical, and electronic properties of the material, e.g., turning graphene from a conductor to a semiconductor [24], or even an insulator in the fully loaded case, called “graphane.” To determine the possible experimental reach, it is, however, crucial to understand the effects that solid-state phenomena have on the β process. These can be essentially classified into two classes: (i) by localizing tritium in the vicinity of a carbon site, its wave function will no longer be a simple momentum eigenstate, and (ii) the degrees of freedom of the substrate will now actively participate in the reaction. This affects the electron spectrum, making it qualitatively different from the one predicted for the process in vacuum. Together with the high energy resolution expected for PTOLEMY, this introduces conceptual and practical challenges for both the neutrino mass measurement, and for the detection of cosmic neutrinos [17,26–29].¹

From the theoretical point of view, understanding the effects of the substrate on the energy spectra involves combining, in unconventional ways, very different theoretical

approaches and numerical techniques, as those used in two domains which are typically considered as separated: the high-energy domain of elementary particles and the low-energy domain of solid-state physics [31]. This can be understood considering the temporal sequence of events depicted in Fig. 1. The evaluation of the spectrum involves the calculation of the matrix element between the initial state and the state just after the decay [Fig. 1(a)]. The state before the decay can be considered as an electronic ground state of tritium [Fig. 1(b)], a configuration that has been well characterized within the last decades [23,32,33]. In particular, the theoretical studies usually rely on density functional theory (DFT), capable of accurately determining the ground-state properties of graphene in interaction with other elements [34,35], and, therefore, the potential felt by tritium on graphene. In light of this, here we use the standard DFT scheme [36,37], based on the adiabatic approximation for the electrons, to describe the initial state of the system. Similarly, standard DFT can be used to evaluate the state of the system long after the decay, at timescales that are longer than those associated with the relaxation of the electronic structure [Fig. 1(d)], including the long timescale dynamics of the whole system [e.g., the vibrational excitation of the substrate, Fig. 1(e)].

Nonetheless, the extreme nonadiabaticity of the $T \rightarrow He$ transition calls for nonconventional schemes to treat the state right after the decay [Fig. 1(c)]. In particular, we combine the DFT scheme with the so-called “sudden approximation” (see, e.g., Ref. [38]), treating the electronic structure as frozen, we introduce its weaker variant, the “semisudden approximation,” and develop novel dedicated tools to implement them. Using these schemes, we calculate the interaction potentials at different stages of the reaction, and use them to compute the spectrum of the outgoing electron, accounting for the possible excitations in the final helium. Our innovative multimethodological approach combines advanced applications of DFT

¹Conversely, it could provide an advantage in looking for keV-scale sterile neutrinos [30].

together with a full quantum treatment of the nuclear states, used for the determination of the decay spectra. This poses the basis for the in-depth study of β decay in the presence of a solid substrate, which is both conceptually new and phenomenologically relevant for future neutrino experiments.

This paper is organized as follows: In Sec. II, we describe the procedure to calculate the β decay rate in the presence of a substrate. Section III reports the calculations of the interaction potentials between the initial state tritium and the substrate, exploiting a standard DFT scheme. Section IV, instead, describes the interaction of helium with the substrate right after the decay, exploiting the sudden approximation, and also reporting a detailed explanation of the nonconventional DFT calculations needed in this context. Finally, in Sec. V, we discuss the actual calculation of the decay rate including the effects of the binding potentials of both tritium and helium, followed by Sec. VI, describing the dynamical evolution on the longer timescales after the decay. We conclude with a summary, and a discussion of the limitations and perspectives of our approach.

Conventions. Unless otherwise specified, we work in natural units, $\hbar = c = 1$, as well as Gaussian units, $4\pi\epsilon_0 = 1$.

II. GENERAL APPROACH TO THE β -DECAY RATE

When a tritium nucleus is bound to graphene, its physical state is described by a wave function, say $\psi_{i,T}(\mathbf{x})$, belonging to the discrete spectrum of its binding potential, with $\mathbf{x}$ being its position. After the decay has happened, the outgoing electron and antineutrino will belong to the continuous spectrum, and their wave functions can be approximated by simple plane waves² $\psi_e(\mathbf{x}) = e^{ip_e \cdot \mathbf{x}}/\sqrt{V}$ and $\psi_\nu(\mathbf{x}) = e^{ip_\nu \cdot \mathbf{x}}/\sqrt{V}$, where we assume to be working at some finite volume V . The state of the final helium nucleus, instead, will be described by a wave function $\psi_{f,He}(\mathbf{x})$ which can belong to either the discrete or the continuous spectrum of the final-state Hamiltonian.

At long enough distances, the weak-interaction Hamiltonian which induces the β decay is local, and its expression in position basis is given by

$$\langle \mathbf{x}_{He}, \mathbf{x}_e, \mathbf{x}_\nu | H_w | \mathbf{x}_T \rangle = g \delta^{(3)}(\mathbf{x}_{He} - \mathbf{x}_T) \delta^{(3)}(\mathbf{x}_e - \mathbf{x}_T) \times \delta^{(3)}(\mathbf{x}_\nu - \mathbf{x}_T), \quad (3)$$

with the obvious definition of the position vectors. The coupling g is related to the microscopic theory of weak interactions, as reported, for example, in Refs. [17,39].

In light of this, the β -decay event rate for a single tritium can be obtained from Fermi's golden rule as

$$d\Gamma = 2\pi \sum_f |\mathcal{M}_f|^2 \delta(E_i - E_f - E_e - E_\nu) \frac{V d\mathbf{p}_e}{(2\pi)^3} \frac{V d\mathbf{p}_\nu}{(2\pi)^3}, \quad (4)$$

²Since the electron is charged, there might actually be long-distance Coulomb effects which distort its wave function. The inclusion of these requires the knowledge of the electric field generated by the tritiated graphene layer at long distances, and it is beyond the scope of the present work.

where E_i , E_f , E_e , and E_ν are respectively the energies of the initial tritium, of the final helium, of the electron, and of the antineutrino. The sum is over all possible final states for the helium nucleus. The matrix element for a given final state simply reads

$$\mathcal{M}_f = \frac{g}{V} \int d\mathbf{x} \psi_{i,T}(\mathbf{x}) \psi_{f,He}^*(\mathbf{x}) e^{-i(p_e + p_\nu) \cdot \mathbf{x}}. \quad (5)$$

It is then clear that, to determine the β -decay rate, one must know the wave function of the initial tritium, as well as the wave functions of the possible final states of helium. In turn, this requires an understanding of how both of them interact with the underlying graphene, before and after the decay has happened. The work presented in the following sections is devoted precisely to this. In particular, we highlight that in earlier studies [17] it was essentially assumed that the interactions of tritium and helium with graphene were essentially the same. Our work revises this assumption by studying how graphene systems respond to the change in the nuclear charge. We will get back to the decay rate and its evaluation in Sec. V.

Before moving on, let us stress right away that the rate presented in Eqs. (4) and (5) cannot be considered as the end of the story. In fact, it does not account for the possible initial- and final-state contributions coming from, for example, the electronic and vibrational degrees of freedom characterizing the graphene (see, e.g., Ref. [28]). We comment more on this in Sec. VII.

III. TRITIUM BEFORE THE DECAY

We start by studying extensively the initial state of tritium bound to graphene [Fig. 1(b)], for different levels of loading, spatial distribution, and magnetization state (see also Fig. 2). Upstream of the DFT scheme employed to determine the electronic structure, there is the adiabatic approximation for the electrons (see, e.g., Ref. [44]). Briefly, the very large ratio between the electron and nuclear masses allows us to consider the electronic state as adiabatically following the nuclear motion. In other words, one solves for the electronic structure for any given nuclear configuration, defining electronic eigenstate energies which are parametrically dependent on the nuclear position, $E_n(\{\mathbf{X}\})$. These eventually provide effective potential-energy surfaces (PESs) for the nuclear dynamics, one for each given electronic state, n . This framework—the so-called Born-Oppenheimer (BO) approximation [45]—is valid under the additional condition that the PES corresponding to different electronic states remain well separated in energy. For hydrogenated graphene, the electronic gap between the ground and first-excited states has been shown to increase with the amount of hydrogenation, up to 5 to 6 eV [24,34,46]. This allows us to safely use the BO approximation for the ground state.

In our case, the ground state PES depends on the coordinates of the tritium and carbon nuclei present in the system, $E_0(\{\mathbf{X}_T\}, \{\mathbf{X}_C\})$. For our purposes, we are interested in the potential felt by a single tritium nucleus, as a function of its coordinate. We define this as

$$U_T(\mathbf{x}) \equiv E_0(\mathbf{x} = \mathbf{X}_{T,1}, \bar{\mathbf{X}}_{T,2}, \dots, \bar{\mathbf{X}}_{C,1}, \bar{\mathbf{X}}_{C,2}, \dots). \quad (6)$$

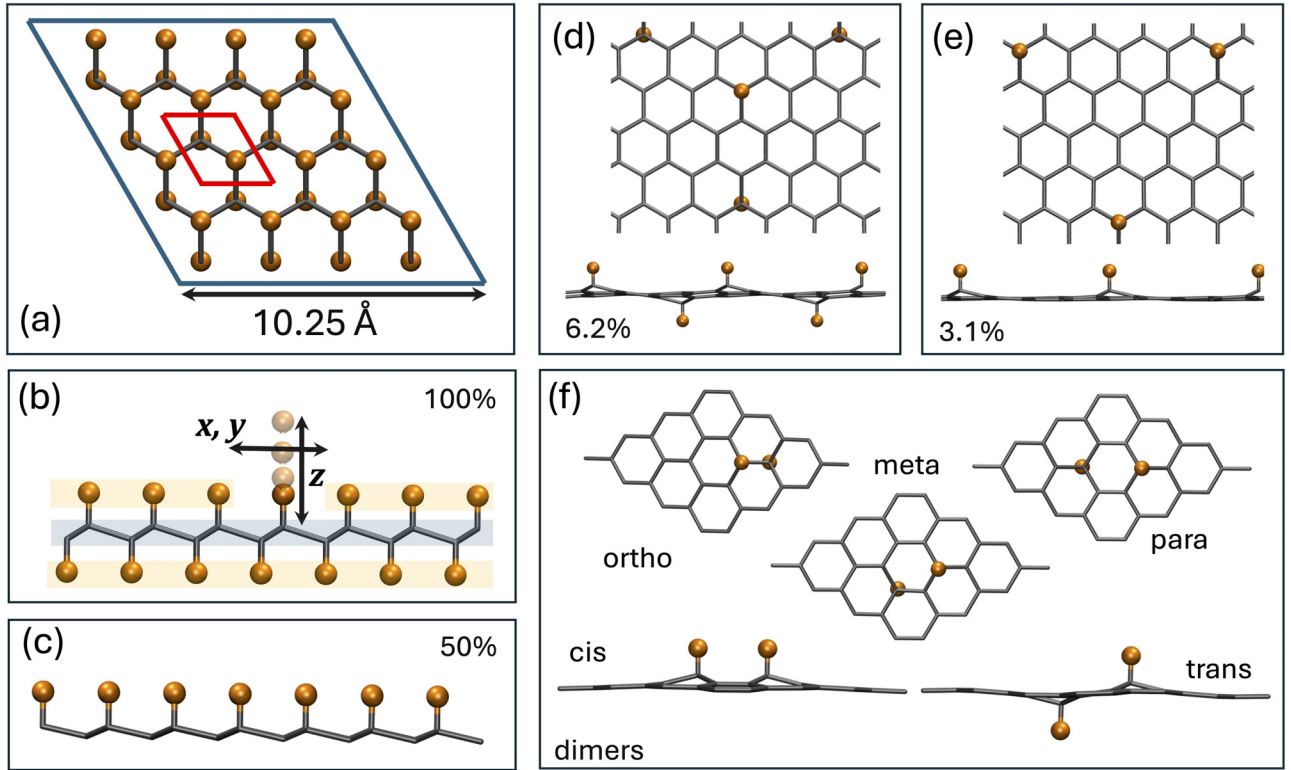


FIG. 2. Model system and calculation setup. The structures include 32 C atoms and up to 32 T atoms and are extended using periodic boundary conditions. The supercell [whose boundaries are in blue in panel (a)] is the 4×4 repeat of the unit cell [in red in panel (a)]. The periodicity in the z direction is 22 Å. The exchange and correlation functional is the Perdew-Burke-Ernzerhof [40] parametrization of the generalized gradient approximation. The core electrons are treated with the projector augmented wave approach and with pseudopotentials [41], and the cutoff for the plane-wave expansion is $k^2/2 = 65$ Ry. Grimme van der Waals empirical corrections [42] are included. The Brillouin zone is sampled with $18 \times 18 \times 1$ symmetrically distributed k points [43]. When structure relaxation is needed [e.g., Fig. 1(a)], we reduce the forces down to 10^{-3} Ry/Bohr. (a) Top view of the fully loaded chair structure. (b) Side view of the same. The coordinates along which the tritium is moved are also reported. In the first prescription for the tritium potential, all other atoms are allowed to relax, in the second one, the carbon ones are kept frozen (gray shaded region), while in the third prescription, the other tritium atoms are also kept frozen (orange shaded region). (c) Side view of the 50% loaded structure. (d), (e) Models of the 6.3% and 3.1% loaded systems. The distance between two tritium atoms is approximately 9.7 Å and 5.6 Å, respectively. (f) Tritium loaded in dimers, in ortho, meta, and para configuration, each considered in cis and trans conformations, as defined in the figure itself.

Given that E_0 is a many-body energy function, the definition above must be supplemented with a prescription on how to treat the other nuclear coordinates $\{\tilde{\mathbf{X}}\}$. Specifically, we consider three possible prescriptions:

- (1) For each value of $\mathbf{x}$, we allow the other coordinates to fully relax to their values corresponding to the lowest-energy configuration. This, however, makes the result very dependent on the environmental factors, such as possible additional restraints that limit the extent of relaxation.
- (2) Since the typical relaxation times are controlled by the ratio M_T/M_C , this implies that the Carbon scaffold [shaded in gray in Fig. 2(b)] relaxes more slowly than the tritium. On short timescales, thus, the carbon nuclei might be kept fixed, allowing only the tritium ones to relax.
- (3) When considering timescales shorter than the vibrational period of the C–T bond (tens of femtoseconds), one is allowed to only vary the coordinate of the

tritium of interest, with all the other nuclei kept frozen. This option has the advantage of being independent of environmental factors.

In the rest of this work, we considered the latter option as the preferred one, although, in some specific cases, all three options are evaluated and compared. Additional details are reported in the Supplemental Material (SM), Sec. SM.I [47].

A. DFT calculations setup and model systems

Within the DFT scheme, the electronic structure and ground-state energy are calculated by solving the Schrödinger equation for single electrons within a self-consistent potential depending on the electronic density, the so-called Kohn-Sham scheme [48]. For our purposes, it is useful to separate the ground-state energy into three terms, with different dependencies on the electron density and nuclear positions, namely,

$$E_0[n, \{\mathbf{X}\}] = E^{\text{int}}[n] + E^{eN}[n, \{\mathbf{X}\}] + E^{\text{NN}}(\{\mathbf{X}\}), \quad (7)$$

whose explicit expressions are given in the SM, Sec. SM.I [47]. Here E^{int} includes the electron kinetic energy and electron-electron interactions, and is a functional of the ground-state electronic density $n(\mathbf{x})$ only. Moreover, E^{eN} is the direct Coulomb integral between the electronic charge and the nuclear charges, explicitly depending on both n and $\{X\}$, while E^{NN} is the interaction among nuclei and depends only on the nuclear coordinates. Within the standard DFT framework, $n(\mathbf{x})$ is determined self-consistently for any given nuclear configuration and therefore depends implicitly on $\{X\}$.

The practical implementation of the DFT scheme requires specifying the functional forms of $E_0[n, \{X\}]$, which are known for E^{eN} and E^{NN} , but not entirely for E^{int} : The exchange and correlation functional, i.e., the part of electron-electron interaction exceeding the direct Coulomb (Hartree) term, is not exactly known, although several approximate forms are available. Here, we choose the generalized gradient approximation in the parametric form of Perdew-Burke-Ernzerhof [40], well tested on similar systems [17,34,49] and displaying high accuracy on hydrogen dissociation [50].

The potential U_{T} defined in Eq. (6) has been computed for the different levels of tritium loading, obtained by spatially distributing it as illustrated in Fig. 2. For the cases of 100% and 50% loading [Figs. 2(a), 2(b) and Fig. 2(c), respectively], we chose symmetric distributions, such that alternate sublattices are occupied on opposite sides (for the 100% case, also called the “chair” conformation) or on a single side (for the 50% case). These conformations, although among the most stable, are considered representative of ideal reference cases. In real systems, more disordered distributions might be entropically favored, especially when ripples or defects are already present [32,51], which tend to clusterize hydrogenation. While here we are forced to regular distributions by the periodic boundary conditions, we note that the binding energy depends on the local occupancy around the site under consideration [34]. Thus, these distributions may also be considered representative of a lower level of loading in the presence of clusters. Much lower levels of loading are here represented arranging fewer tritium atoms in evenly spaced positions [Figs. 2(d) and 2(e) for 6.2% and 3.1%, respectively], or in “dimers,” i.e., adjacent locations [Fig. 2(f)]. In most instances, the calculations are performed without restriction on the electronic spin state in order to detect possible magnetic states, while in some cases the spin has been restricted to a direction orthogonal to the graphene sheet, to emulate the presence of an external magnetic field.

Calculations were performed with QUANTUM ESPRESSO v7.2 [52]. Input preparation and output analysis were performed with XCRYSDEN [53] and VMD [54].

B. The tritium orthogonal potential

For each of the prescriptions described in Sec. III, we evaluate the tritium potential as a function the z coordinate, perpendicular to the sheet, with x and y , the coordinates parallel to it, kept fixed,

$$U_z(z) \equiv U_{\text{T}}(x = 0, y = 0, z). \quad (8)$$

In most cases, the qualitative shape of the potential is similar, and exemplified by the potential of extraction of an isolated tritium [Fig. 3(c)]. It displays a minimum with energy U_0 , at $z_0 \simeq 1.1 \text{ \AA}$,³ a deep rise for $z < z_0$ (i.e., when the tritium gets closer to the carbon), and a softer rise for $z > z_0$, culminating in a maximum of energy U_b , located at z_b . This defines a desorption energy barrier, $E_d \equiv U_b - U_0$. After the barrier, at large z , the energy may decrease to a final value, U_f , defining a barrier for the inverse adsorption process, $E_a \equiv U_b - U_f$. The depth of the binding potential is, instead, defined as the difference $E_b \equiv U_0 - U_f = E_a - E_d$, and is negative if bound states are allowed [see again Fig. 3(c)]. Given this qualitative behavior, however, the value of the barriers depends on the level of loading and on the spatial distribution of tritium, as well as on the magnetization state of the system. In some instances, there might even be multiple barriers, or none at all. The energies E_b , E_d , and E_a , as well as other parameters, are reported in the supporting Table SM.1 [47], for all cases studied.

Let us now describe some specific cases more in detail. Figure 3(a) reports the orthogonal potential U_z evaluated at 100% loading. Looking at the binding minimum, one can see two main groups of curves having low and high values of U_0 , separated by $\approx 4 \text{ eV}$. The lower-energy curves are obtained by leaving the magnetization of the system free to adjust spontaneously, while the higher-energy curves are obtained by restraining the magnetization to $M = 2\mu_{\text{B}}$, where μ_{B} is the Bohr magneton. When the magnetization is free, the preferred one for the tritium bound state is $M = 0$ (spin singlet, the solid part of the curves). However, as tritium is extracted, it drags its single electron away from the substrate, preventing it from coupling with another one to form a singlet state. Therefore, when this happens, the system displays a magnetization $M = 2\mu_{\text{B}}$ (dashed part of the curves), which is due both to the spin of the electron pertaining to the detached tritium, and to the spin of the dangling bond. The spin density of the latter distributes around the vacancy on the substrate, as shown by the top view of the structure reported in Fig. 3(a) (red sites = spin up, blue sites = spin down). If, on the other hand, the magnetization is forced to be $M = 2\mu_{\text{B}}$ along the whole path (all dashed curves), the energy of the binding minimum increases by $\approx 4 \text{ eV}$. This also implies a decrease in the depth of the potential as compared with the case of free magnetization, from $|E_b| \simeq 4.3 \text{ eV}$ to $|E_b| \simeq 0.5 \text{ eV}$. Similarly, the desorption energy decreases from $E_d \simeq 4.3 \text{ eV}$ to $E_d \simeq 1.5 \text{ eV}$ (see also Table SM.1 [47]).

Within the two main groups of curves are minor differences concerning the location and height of the barriers. Specifically, allowing for an increasing amount of relaxation of the other nuclei produces a lowering of the energy profiles in the region $2 \text{ \AA} \lesssim z \lesssim 4 \text{ \AA}$, as well as a disappearance of the small adsorption barrier (see the difference between differently colored curves, as detailed in the caption, and Table SM.1 [47] for the numerical values).

³The origin, $z = 0$, is taken as the location of the carbon nucleus to which tritium is bound, so that z is the length of the T-C bond.

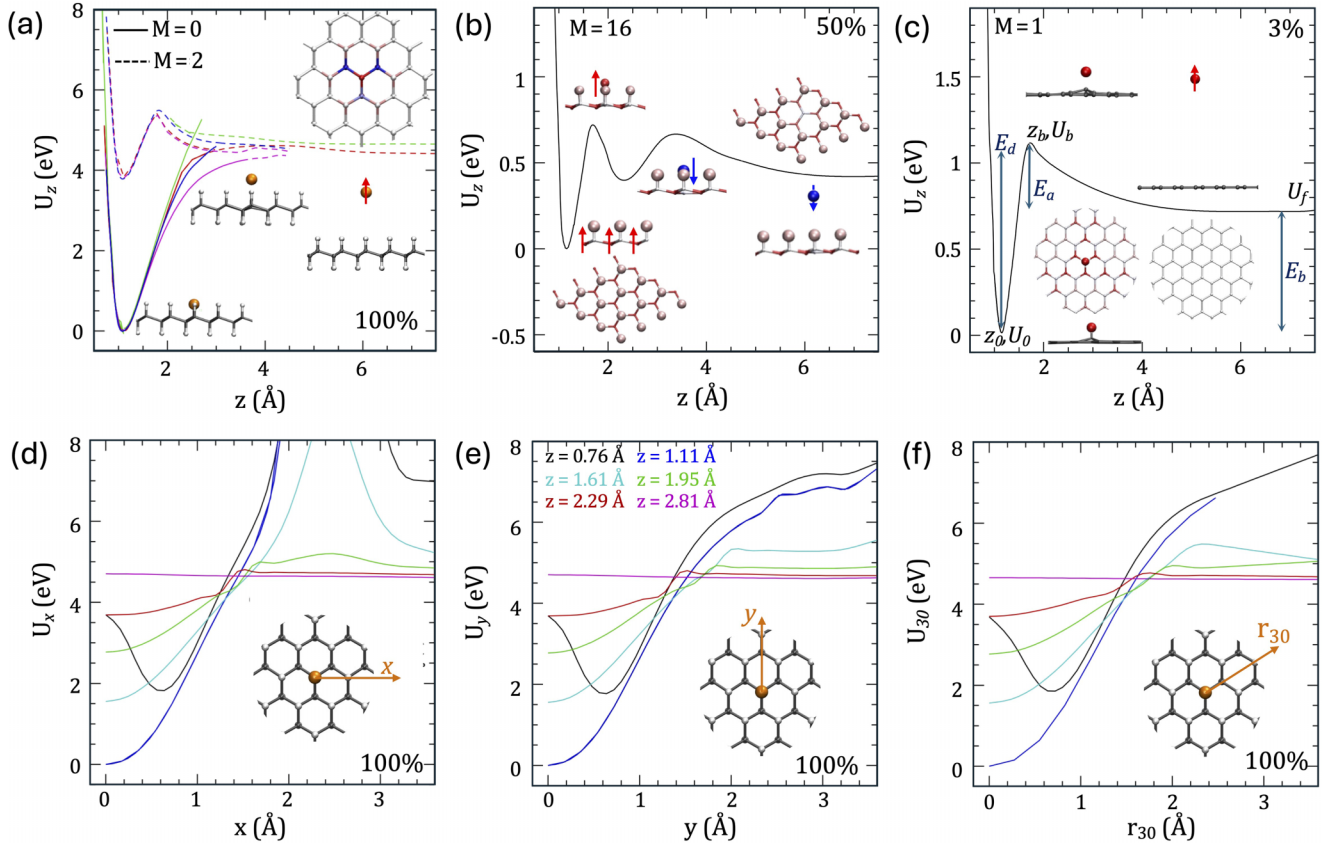


FIG. 3. Sample orthogonal and parallel potentials. (a) U_z at 100% loading. Solid and dashed lines correspond to different magnetization of the system, as indicated in the legend, while different colors correspond to different conditions for the relaxation of nuclei. Specifically, red and green are obtained by slowly dragging the tritium under consideration and relaxing the rest of the system during dragging, either keeping fixed only the carbon nucleus right below (red), or all carbon nuclei (green). Magenta lines are obtained by fixing the C-T distance at evenly separated values along the path of the tritium and relaxing all the rest, while, for the blue line, all carbons are kept fixed in their starting position (more details on the calculation are reported in SM.III.A). Side views of the structures in the minimum, barrier and detached states are reported under the plots. A top view of the system (unbound state) is also reported, colored according to the local magnetization (red for spin up, blue for spin down). (b) U_z computed at 50% loading with symmetrically distributed tritium, evaluated with free magnetization, which turns out to be $M = 16\mu_B$ ($1\mu_B$ per unit cell), and with the full relaxation prescription. The structures, located near their corresponding place along the curve, illustrate the distribution of magnetization, with coloring as in panel (a), and the arrows indicating the direction of the spin. (c) U_z for the case with lowest loading. Side and top views of the structures are also reported, colored according to magnetization as in the previous panels. We also show the definitions of the various energies and special positions discussed in the main text. (d)–(f) Parallel potentials for 100% loading, with as a function x , y , and a direction at 30° from the horizontal one, as indicated in the structures shown in each panel. The different colors correspond to different values of the z coordinate, fixed at different heights, as indicated in the legend of panel (e). The potentials are evaluated with all nuclei kept fixed except the tritium under consideration.

Although the ground-state magnetization is generally null, there are some exceptions. These happen when the atoms are spatially distributed in particularly symmetric configurations, as dictated by the symmetries of the graphene lattice. This can be seen as the union of two triangular sublattices. In the case of 100% loading, half of the tritium atoms are bound on one side of the sheet, on one of the sublattices, and the other half on the other side, and on the other sublattice [see Fig. 2(a)]. When the system is magnetized, spins on adjacent sites tend to have opposite directions and therefore same-direction spin tend to occupy alternate sites, i.e., to be on the same sublattice. This is shown in the top view of the structure reported in Fig. 3(c). The Tritium generates magnetization on the sheet on alternate sites around its own (sites with spin up density are colored in red), and similar situations occur when the

symmetry of the bound tritium atoms is favorable (see structures reported in Table SM.1 [47]).

The case of 50% loading we consider here, with tritium loaded on a single side and on alternate sites, is especially favorable to magnetization, since all the sites of a given sublattice are occupied and all those of the other are empty. Because of this, the unpaired electrons are all on the same sublattice and tend to align their spins, producing a macroscopic magnetization ($M = \pm 1\mu_B$ for each unit cell), with a gain in energy with respect to the nonmagnetic state of ≈ 0.23 eV/unit cell. On the other hand, the tritium binding is looser than in the fully loaded case [see Fig. 3(b)]. Furthermore, when the tritium detaches and carries away an unpaired electron with itself, spin rearrangements are needed, which produces multiple barriers. The barrier observed for the detachment

of an isolated tritium at low coverage [Fig. 3(c)] is due to similar spin rearrangements: in the bound state, the additional electron induces a spin-density distribution in alternate sites around tritium, as previously noted. Upon detachment, the graphene recovers its spin neutrality.

In summary, there is a marked dependence of the binding and desorption energies on the tritium coverage and distribution, which act both directly, modifying the local structure, and indirectly, producing a spontaneous magnetization in given configurations, which in turn alters the potential profiles. Overall, the values of the desorption energy E_d range roughly from 0.7 to 5.3 eV. The binding energy E_b has a similar spread, in agreement with the literature [32]. However, we observe that the magnetic configuration may be additionally stabilized or destabilized by the presence of external magnetic fields, as those envisioned in PTOLEMY's setup.

C. The tritium parallel potential

To further probe the interaction between tritium and graphene, we also studied how the potential changes when moving parallel to the graphene plane, exploring it along three symmetry directions, namely,

$$U_x(x, z) \equiv U_T(x, y = 0, z), \quad (9a)$$

$$U_y(y, z) \equiv U_T(x = 0, y, z), \quad (9b)$$

$$U_{30}(r_{30}, z) \equiv U_T\left(x = \frac{\sqrt{3}}{2} r_{30}, y = \frac{1}{2} r_{30}, z\right), \quad (9c)$$

while the z coordinate is kept fixed at different values. The results are reported in Figs. 3(d)–3(f), where the symmetry directions are explicitly shown, and the potentials corresponding to different values of the z coordinate are plotted in different colors.

Importantly, in the region of about 1.5 Å around the equilibrium point, the potential is very similar in all three directions, due to the high degree of isotropy induced by the hexagonal symmetry of the graphene lattice. In this region, the curves corresponding to $z < z_0$ (black line) display repulsion at $x = y = 0$, since the C–T bond is compressed. Conversely, all the other curves display an attractive minimum, which becomes shallower as the distance between tritium and graphene increases, as expected.

For displacements larger than 1.5 Å, instead, large anisotropies appear. In particular, U_x presents a large potential barrier [see, again, Fig. 3(d)], since moving in that direction, the tritium encounters another one bound in meta position at $x = 2.5$ Å. In the case of U_y and U_{30} , instead, the nearest tritium is located at 4.3 Å, and therefore the barrier is considerably farther away, out of the range probed here. These results, together with the potential U_z described in the previous section, give a good description of the complete potential, $U_T(\mathbf{x})$, for 100% loading. This will serve as the basis to compute the initial-state wave function to be used in the β -decay rate, as anticipated in Sec. II and detailed in Sec. V.

IV. HELIUM RIGHT AFTER THE DECAY

We now move to the analysis of the final state of the reaction in Eq. (1): Helium in interaction with the rest of the substrate immediately after the decay. Near the end point, the β decay happens over a timescale of about $t_\beta \approx 10^{-18}$ s, which is conservatively estimated as the time it takes for the β electron with momentum $p_\beta \approx 100$ keV to escape the helium atom, whose radius is $r_{\text{He}} \approx 1$ Å.

Immediately after the decay, the electronic structure will still be the one corresponding to the ground state of the system before the decay. However, for the new system, which now has a helium nucleus, this will not correspond to the ground state anymore but rather a combination of excited electronic states [named He^* in Fig. 1(c)]. The time it takes for this state to relax down to the ground state is very variable, depending on the specific mechanisms of nonadiabatic relaxation, but it is generally not smaller than $t_r \approx 10^{-16}$ – 10^{-14} s [55,56]. We can then safely assume $t_\beta \ll t_r$. This circumstance evidently prevents the use of the BO approximation, which requires that the electronic structure corresponds to an eigenstate of the current nuclear configuration.

In this context, one often uses the so-called sudden approximation (see, e.g., Refs. [57,58]). In our case, such an approximation is valid because, on the timescale relevant for the decay, the electronic structure of the system does not have enough time to relax, thus remaining the same as it was right before the transition. However, the implementation of this approximation in our context requires abandoning the standard DFT scheme. Specifically, referring to Eq. (7), the electronic density, $n(\mathbf{x})$, should not be calculated self-consistently given the new nuclear configuration (with a helium) but must be kept the same as it was before the decay. As a consequence, the term $E^{\text{int}}[n]$ in Eq. (7) is the same as the one evaluated before decay. Conversely, the terms $E^{\text{NN}}(\{X\})$ and $E^{\text{eN}}[n, \{X\}]$ do vary, since the nuclear charge has now changed. The calculation of these nonself-consistent terms is not implemented in standard DFT and therefore require specific postprocessing tasks, which we describe in the SM, Sec. SM.I.E [47].

Even within the sudden approximation, the final helium potential depends on the choice we make for the electronic density n .⁴ In particular, we implement two possible choices, whose results are reported in Fig. 4(a).

- (1) *The very sudden approximation.* The electronic density employed to compute the helium potential is the density evaluated before decay, for a value of the tritium coordinate equal to the equilibrium one, i.e.,

$$n(\mathbf{x}) \equiv n_{X_T=(0,0,z_0)}(\mathbf{x}). \quad (10)$$

Since in this case the electronic density is independent of the position of the helium nucleus, and mostly dense near the original equilibrium position, at large distance, the helium is extracted as a naked nucleus He^{++} .

⁴As before, the potentials also depend on how other nuclei are treated. For this case, we use the prescription where all the others are kept frozen.

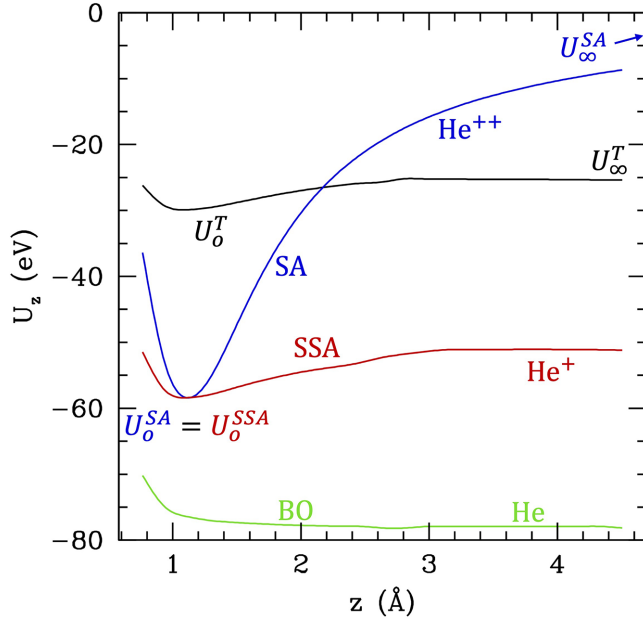


FIG. 4. Orthogonal helium potential in sudden and semisudden approximation (respectively, SA and SSA, in blue and red), and in the adiabatic (BO) approximation (green). The system is considered electrically isolated during decay, and therefore the total charge is $+1$, although in the three cases the helium is extracted in different ionic states, as indicated. The corresponding parallel potentials are reported in Fig. SM.4 [47]. For comparison, the tritium potential is also reported, aligned to a common energy frame as explained in the text and in the SM, Sec. SM.I.F [47].

The corresponding potential is strongly attractive as a consequence of the Coulomb interaction with the negatively charged substrate, as seen in Fig. 4.

- (2) *Semisudden approximation.* In this case, the electronic density is taken to be the same as before the decay, but evaluated at a tritium coordinate equal to the current helium coordinate,

$$n(\mathbf{x}) \equiv n_{X_T=X_{\text{He}}}(\mathbf{x}). \quad (11)$$

In this case, it turns out that a single electron follows the helium nucleus. Consequently, for large distances one actually extracts a He^+ ion, and its potential is less attractive than in the sudden case.

In Fig. 4, we also report the helium potential obtained within the full adiabatic approximation (i.e., the standard BO framework). In this case, two electrons follow the helium nucleus, which detaches from the substrate as a neutral atom. As a noble element, an unbound helium atom is very stable, and therefore its potential is repulsive. The vertical displacement of the adiabatic curve with respect to the sudden or semisudden potential at their minima is due to the electronic structure relaxation, and turns out to be approximately 18 eV. The figure also includes the adiabatic potential for tritium. Within DFT calculations, the absolute energy reference of systems with different constituents is generally different. Consequently, to correctly align the tritium potential to the others, we used as reference the Coulomb tails of potentials for the

helium and tritium nuclei. These are aligned using the respective sudden potentials (that for tritium is not shown here, but has been computed for this purpose). More details are given in the SM, section SM.I.F [47]. This sets the energy difference between the minimum of the tritium potential and the minimum of the sudden or semisudden potentials to be $U_0^T - U_0^{SA \text{ or } SSA} \simeq 29$ eV.

Which of these potentials one should use is a matter of timescales. As mentioned, the sudden approximation assumes that the electronic density is the same as it was when the tritium occupied its equilibrium position before the decay. However, at least from a semiclassical viewpoint, the helium nucleus employs some finite time to probe larger distances. If this time exceeds t_r , the electronic structures may have time to relax, consequently changing the potential felt by the helium itself. Moreover, our semisudden approximation is inspired by a semiclassical picture where the tritium is slowing moving around, with its motion followed adiabatically by the corresponding electronic density. When it suddenly decays, at a given position X_T , the electronic density remains frozen to the configuration it had for that position. Therefore, if $t \ll t_r$, the potential is expected to be something in between the sudden and semisudden case, with the former providing a better description of the regions near the minimum, and the latter for the regions farther away. For much longer times and distances, instead, the electrons will relax, and the repulsive adiabatic potential will gradually provide a better description.

V. THE β -DECAY RATE

We now have all the ingredients to determine the β -decay rate following from Eqs. (4) and (5). The wave function of the initial tritium, $\psi_{i,T}$, is taken to be in the ground state of the initial potential, while the wave function for the final helium nucleus, $\psi_{f,\text{He}}$, is evaluated starting from the potentials determined within each of the three schemes described in Sec. IV: sudden, semi-sudden, and adiabatic. As we will see, each of these schemes results in a different shape for the β -electron spectrum.

Our starting point to determine the wave functions, both initial and final, is the generic form of the Schrödinger equation for the nuclei participating in the decay process,

$$-\frac{1}{2m} \nabla^2 \psi_A(\mathbf{x}) + U(\mathbf{x}) \psi_A(\mathbf{x}) = \varepsilon_A \psi_A(\mathbf{x}), \quad (12)$$

where m is either the tritium or the helium nuclear mass, and A is a set of quantum numbers. Depending on whether one is solving for the initial or final wave function, the potential U is either of the potentials described in the previous sections.

We first recall that, in the bound region, i.e., for energies $\varepsilon_A < U_f$, the potentials reported in Fig. 3 (and Fig. SM.4 [47]) look approximately the same if computed as a function of the three parallel directions we probed. Large anisotropies only appear for distances sufficiently away from the minimum, as commented in Sec. III C. These regions however, give a minor contribution to the matrix element in Eq. (5), since the initial tritium wave function is exponentially localized in the vicinity of the minimum. This allows us to approximate the tritium and helium potentials as isotropic on the graphene plane,

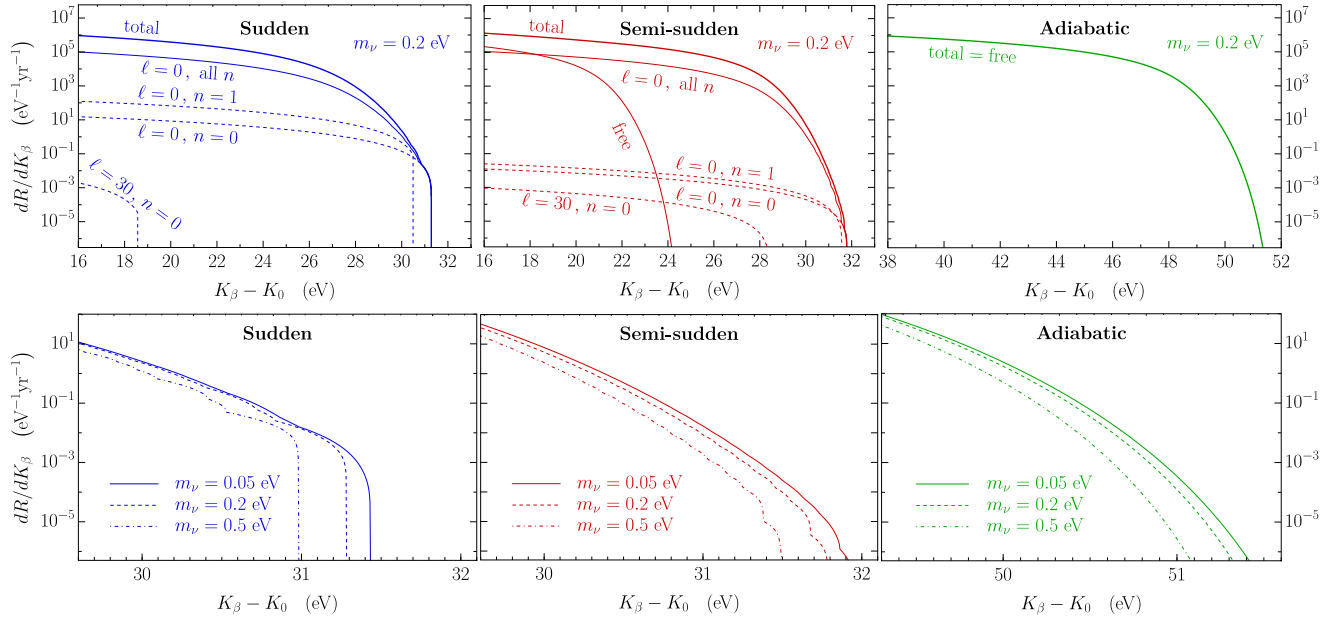


FIG. 5. Electron β -decay spectra obtained for each of the three schemes employed to define the final helium potential. The initial tritium potential is taken to be the one corresponding to 100% loading, computed in the prescription where all other nuclei are kept fixed (see Sec. III). The total tritium mass is taken to be $M_{\text{tot}} = 1 \mu\text{g}$. The electron's kinetic energy is measured with respect to the end point of a tritium nucleus in vacuum and for a massless neutrino, K_0 . (upper panels) Total rate for $m_\nu = 0.2 \text{ eV}$. We also show the partial contribution for some selected final states (or groups of final states), as indicated directly in the figures. (lower panels) Total rates in a region much closer to the end point, as computed for different values of the neutrino mass.

$U(\mathbf{x}) \simeq U(r, z)$. If one is considering a bound state, the dependence of its wave function on the polar angle defined on the graphene plane, θ , is then completely determined to be

$$\psi_{n\ell}(\mathbf{x}) = \chi_{n\ell}(r, z) \frac{e^{i\ell\theta}}{\sqrt{2\pi}}, \quad (13)$$

with $\ell \in \mathbb{Z}$. The quantum number n labels the bound state solution to the remaining Schrödinger equation,

$$-\frac{1}{2m} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) - \frac{\ell^2}{r^2} + \frac{\partial^2}{\partial z^2} \right] \chi_{n\ell} + U(r, z) \chi_{n\ell} = \varepsilon_{n\ell} \chi_{n\ell}. \quad (14)$$

The initial state of tritium is assumed to be the ground state of the potential described in Secs. III B and III C, so that the wave functions describing the tritium and a generic helium bound state are

$$\psi_{i,T}(\mathbf{x}) = \frac{\chi_{00}^T(r, z)}{\sqrt{2\pi}}, \quad \psi_{f,\text{He}}(\mathbf{x}) = \chi_{n\ell}^{\text{He}}(r, z) \frac{e^{i\ell\theta}}{\sqrt{2\pi}}. \quad (15)$$

For final states where the helium is, instead, in the continuous spectrum (i.e., when it is freed from the graphene right after the decay), we simply approximate the wave function by a plane wave. The details on how we solve the Schrödinger equation and how we compute the event rates are reported extensively in the SM, Sec. SM.II [47].

In Fig. 5, we report the resulting electron spectra, as obtained for a total tritium mass of $M_{\text{tot}} = 1 \mu\text{g}$, corresponding to about 2×10^{17} tritium atoms. For the sake of this work, we consider the simpler instance of a single neutrino species, with mass m_ν . In the upper panel we give an extended view

of the partial contributions coming from various final states, for $m_\nu = 0.2 \text{ eV}$. In the lower panel, instead, we enlarge the end-point region, and show how the expected rate changes with varying neutrino mass.

As one can see, the different schemes for the determination of the final helium potential produce β -decay spectra that share some similarities, but also some differences. In particular, both the spectra obtained within the sudden and semisudden schemes show several features in the near-end-point region, each associated with the contribution due to a different bound state that the helium nucleus can end up in. These are very characteristic of the system that hosts the decaying nucleus, thus differentiating the rate expected for a setup like KATRIN [13], PTOLEMY [15], or Project8 [19].

Nonetheless, the rate obtained with different schemes, differ in a few ways. First of all, when final helium bound states are allowed, the maximum electron energy is

$$\begin{aligned} K_\beta^{\text{end}} &\equiv Q - m_\nu + \varepsilon_{00}^T - \varepsilon_{00}^{\text{He}} \\ &= Q - m_\nu + U_0^T - U_0^{\text{He}} \\ &\quad + \frac{1}{2}(\omega_t^T - \omega_t^{\text{He}}) + (\omega_p^T - \omega_p^{\text{He}}), \end{aligned} \quad (16)$$

where $Q \equiv m_T - m_{\text{He}} - m_e$ is the Q value determined by the tritium and helium nuclear masses, and ε_{00}^T and $\varepsilon_{00}^{\text{He}}$ are the energies of the ground state of tritium and helium, respectively. In the last line we have expressed these energies in terms of the parameters of the potentials, in particular, the value of their minima, U_0 , the fundamental frequency in the direction transverse to the graphene, ω_t , and the fundamental frequency in the direction parallel to the graphene, ω_p . Now, while the

minimum of the potential is the same for both the sudden and semisudden schemes, the fundamental frequencies are not, because they depend on the actual shape of the potential close to its minimum.

The two schemes also differ in the separation between the end point and the onset of the contribution coming from the helium continuous final states. In fact, the energy at which the helium can be freed from the graphene layer is determined by the difference between the energy of the initial bound tritium, and the value taken by the helium potential at infinity, U_{∞}^{He} . Specifically, it is given by

$$\begin{aligned} K_{\beta}^{\text{free}} &\equiv Q - m_v + \varepsilon_{00}^T - U_{\infty}^{\text{He}} \\ &= Q - m_v + U_0^T + \frac{1}{2}\omega_t^T + \omega_p^T - U_{\infty}^{\text{He}}. \end{aligned} \quad (17)$$

Since the value of the potential at infinity is much lower for the semisudden approximation than it is for sudden approximation, the onset of the continuum in the former is substantially closer to the end point than it is for the latter.⁵ For energies sufficiently far from the end point (but not so far that the neutrino momentum can no longer be neglected), the contribution coming from continuous final states might dominate the total decay rate, and consequently the experimental statistics.

Finally, the spectra associated with each final bound state (some of them shown as dashed lines) are more widely separated in the sudden case. This is because the potential well is narrower, thus causing a wider separation between energy levels. The latter quantity is the one setting the distance between the various end points of the partial rates associated with different helium bound states.

For values of the electron energy sufficiently below the end point, the features mentioned above are not visible anymore. This is because the various discrete final states get denser and denser, effectively making the difference between each other vanishingly small.

Lastly, in the adiabatic scheme the final helium potential is purely repulsive and, therefore, does not allow for bound states. Consequently, the electron spectrum gets contributions only from the continuous final states.

Before moving on, we highlight a crucial fact. The PTOLEMY project aims for an energy resolution of about 100 meV. As compared with that, the difference between the end-point energies we are predicting here and the one expected in vacuum is extremely large. This constitutes a clear, experimentally measurable signature of the fact that the presence of a solid-state substrate has consequences on the β -decay spectrum.

VI. THE FATE OF HELIUM

After the nuclear reaction, when both the β electron and the antineutrino are far away, the system is left with helium in place of tritium, in an excited electronic state, and will tend to relax to the new electronic ground state. Figure 1(d) reports a view of the electronic density rearrangement upon

this relaxation, determined by comparing the electronic density $n(\mathbf{x})$ evaluated right before the decay with the tritium in its equilibrium position, $\mathbf{z}_0$, with that evaluated after full electronic relaxation with the helium also in $\mathbf{z}_0$. We find that the electrons deplete the light blue areas and populate the pink ones (a top view of the same figure is reported in the SM Fig. SM.1 [47]). This is simply understood, as they tend to move toward the helium nucleus, to partially compensate for its additional positive charge. After electronic relaxation, the BO approximation can be safely used again. In the simulations reported here, however, we further assume that the energy that the helium nucleus has possibly acquired from the nuclear reaction, is small or dissipated during the time t_r , during which the attractive sudden potential lives (the opposite situation, in which the helium nucleus is freed right away from the sheet, is considered in Ref. [59]). The potential calculated in the BO approximation (Fig. 4, blue line) pertains to the neutral atom and is repulsive. Consequently, helium is eventually released from the structure. We explore the release and the following motion of the substrate performing BO molecular dynamics, i.e., solving the classical motion on the ground-state PES.

Figure 6(a) reports the dynamics of the system for the first picosecond, starting from the equilibrium configuration before the decay with null velocities (i.e., roughly zero temperature). We have studied the dynamics of the system for two different configurations: electronically isolated from the outside, and grounded. The red curves in Fig. 6 correspond to the first instance, in which the system has a total charge of +1, while the black curves correspond to the second instance, where the system is neutralized by gaining an electron from the outside. We find that the helium detaches in few fs with an energy gain for the system >2 eV, as expected (numerical values of these energies for different cases are reported in the SM, Fig. SM.1 [47]). The oscillations which are visible in Fig. 6 are due to the vibrational excitations induced by the recoil of the carbon site on which the decay has happened, shown in the structure reported in the inset. When the system is neutral (black lines), the behavior is similar, but the energy gain is nearly double as a consequence of the larger stability of neutral system.

Just after release, the total kinetic energy gets a contribution due to the velocity acquired by the helium, which is $v_{\text{He}} \approx 2.9 \times 10^{-5} \simeq 0.088 \text{ \AA/fs}$, for the overall charged case, and $v_{\text{He}} \approx 5 \times 10^{-5} \simeq 0.15 \text{ \AA/fs}$, when the system is electrically neutral. These values correspond to a helium kinetic energy of about 1.2 and 3.5 eV, respectively. As the system evolves, helium bumps on the graphene layers and gradually distributes its energy to the substrate over a timescale of ps. This is shown in the upper part of Fig. 6(b), where we also show a prototypical trajectory in the inset. As a consequence, the average energy of the system increases of a few eV.

While these energies and temperatures might seem very high, one must consider that the simulations are performed with a small supercell of area $\lesssim 1 \text{ nm}^2$, periodically repeated. This means that we are not actually observing a single helium release, but rather the simultaneous release of periodically spaced helium atoms, about 1 nm apart from each other. Each of them is increasing the system energy by a few eVs. As one can see from the rough relaxation time of the curves in

⁵Indeed, for the sudden case, the onset of the continuous states is so far from the end point that it does not show in our plot.

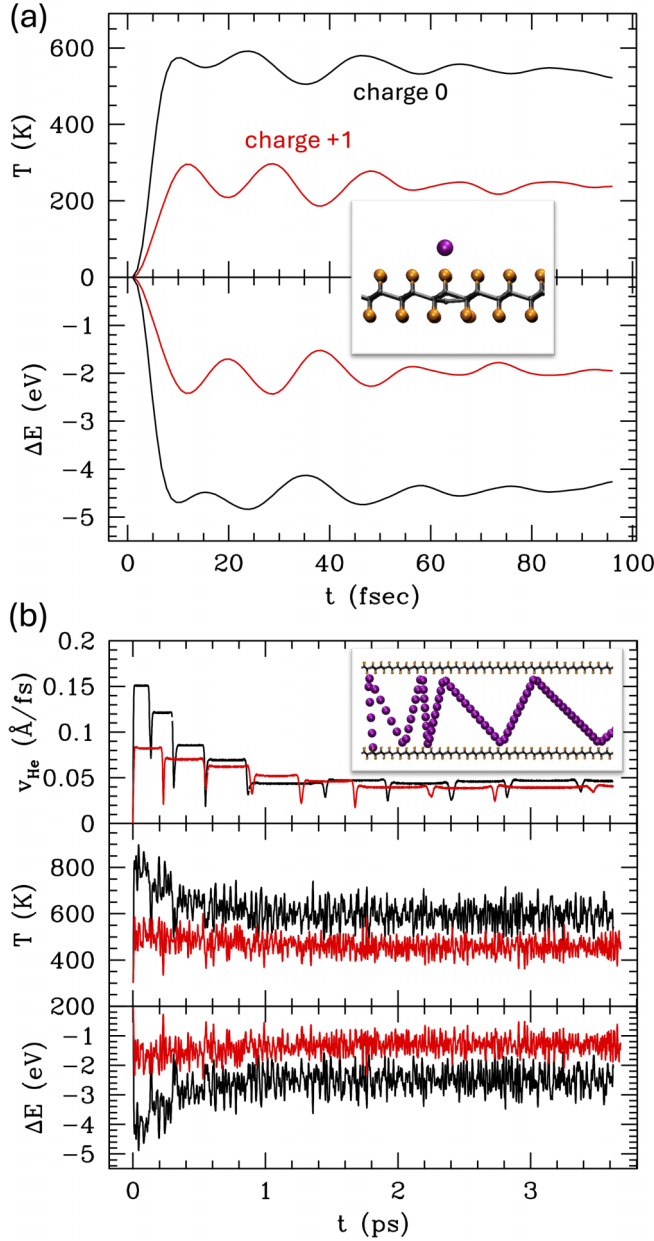


FIG. 6. Evolution of $\Delta E \equiv E_0(t) - E_0(t = 0)$, temperatures and helium velocities with BO molecular dynamics after the nuclear decay. In both cases the black curves are obtained, neutralizing the system with an additional electron to compensate the additional positive charge of helium. The red ones are instead for an electrically isolated system, which then carries a global charge of +1. Given a certain kinetic energy of the nuclei, K , the temperature is defined by $K \equiv \frac{3}{2} N k_B T$, with $N = 32$ the number of carbon atoms in the supercell. (a) the starting configuration is the one in equilibrium before decay, and the starting velocity is null. The structure reported as inset shows that the C site where He is detached is deformed by recoil. (b) the starting configuration is the same and the velocities are randomly distributed to set the starting temperature at 300 K. In this case, we also report the helium velocity, in the top plot. A representation of the helium trajectory bumping between layers is also reported (helium in purple). The system is evolved with Newtonian dynamics for the nuclei, integrating with the Verlet algorithm and with a time step of 0.97 fs.

Fig. 6, it takes about 1 ps to distribute this energy away to the rest of the system. The total radioactive activity of tritium is $d\Gamma/dM \simeq 3.6 \times 10^{14} \text{ g}^{-1} \text{ s}^{-1}$. For a total mass $M_{\text{tot}} = 1 \text{ } \mu\text{g}$, which is the benchmark considered so far, this implies around one decay every 3 ns, leaving time for the system to cool off.

Nonetheless, we also ran a second set of simulations, where we intentionally put the system in more challenging conditions, to test the possible damaging effects of the released helium—Fig. 6(b). In particular, we set the starting velocities to those corresponding to room temperature, instead of starting with $T = 0$. Even in this context, we do not observe any damage produced by the helium to the structure. Actually, the creation of a vacancy in the carbon substrate, may only happen in very specific cases, when helium hits some weaker bonds of the graphene scaffold frontally and with kinetic energy exceeding $\approx 3 \text{ eV}$. There, weaker bonds are typically located at the boundaries between T-loaded and T-free areas. One such case, created on purpose, is illustrated in the SM, Fig. SM.2 [47]. Overall, our simulations suggest that these events are extremely unlikely.

VII. LIMITATIONS OF OUR APPROACH AND THEORY SYSTEMATICS

As already explained, to successfully constrain the possible values of the neutrino mass it is of utmost importance to provide a reliable theoretical prediction for the electron's β -decay spectrum. The present work is a first step in this direction, as we connect the properties of tritiated graphene to the shape exhibited by the spectrum. The framework we are currently working in, however, has some limitations, which we now discuss.

First of all, we are not accounting for the other possible degrees of freedom which can be excited in both the initial and final states of the reaction. These can be vibrational modes of the substrate or electronic excitations. If present in the initial state, they might contribute to changing the quantum and statistical properties of the decaying tritium nucleus, while, if present in the final state, they will subtract energy and momentum from the outgoing electron, inducing further distortions in its spectrum.

Second, we frame everything in terms of “potentials” for the initial tritium and final helium nuclei. At this stage, this is done to simplify the treatment, by reducing the problem to the quantum mechanics of a single particle. To define a potential like this one, one must, however, reduce the intrinsically many-body nature of the problem to that of a single body. Nonetheless, the nuclear system we are dealing with does not feature any truly large hierarchy between masses and/or timescales to rigorously justify this separation, as of now (see the following section for possible ways out). In light of this, we work under different prescriptions for how to deal with the other nuclear coordinates, as described in Sec. III. Each of these prescriptions comes with advantages and disadvantages and lead to final results that can be different from each other.

However, upstream of the nuclear dynamics there is a strong assumption we made on the separation between electronic and nuclear dynamics, and further treatment of the electronic problem either in the fully adiabatic (BO)

approximation or in its opposite, the (semi-)sudden approximation. While the BO approach is reasonably acceptable before decay and after electronic relaxation, the critical temporal region just after the decay is characterized by a strongly nonadiabatic electron dynamics. In this work, we adopted the “sudden” scheme, which is an extreme simplification valid for the very early instants after the β decay, leading to the definition of a possible potential for helium, accounting for the almost instantaneous change of nuclear charge. Consequently, on top of the standard BO scheme for the calculation of the helium potential, we implemented two additional schemes, corresponding to different declination of the sudden approximation. While combining these schemes with the quantum treatment of the nuclear state for the calculation of the decay rates is one of the most innovative aspects of our work, the systematic applicability of the sudden approximation, as combined with the concept of potential, should be investigated deeply, possibly within a nonadiabatic coupled electron nuclear approach (see next section).

As we reported in the previous sections, the implementation of the different prescriptions and schemes, eventually leads to qualitative and quantitative differences in the final electron spectrum. At this stage, these differences should be taken as a first (very conservative) measure of the theory systematics. This can be practically done, for example, by estimating the sensitivity to the neutrino mass starting from each of the three spectra reported in Fig. 5, and taking their largest different as theory uncertainty.

VIII. CONCLUSIONS AND PERSPECTIVES

The issues raised in the previous section could all be summarized in the consideration that the established and more commonly used theoretical scheme generally relies on some sort of separation of energy or timescales, which in turn allows us to decouple a subset of degrees of freedom from others, facilitating the approach to the problem. In this work, conversely, we aimed at addressing a question which is at the connection point of high- and low-energy scales, overlapping on different timescales, bridging solid-state physics with nuclear physics. Therefore, approaches relying on the separation of degrees of freedom, although they can be used as the starting point, need to be reconsidered and possibly revised.

Specifically, we assumed that the degrees of freedom of the tritium and helium nuclei involved in the decay can be separated from the other degrees of freedom to evaluate the single tritium-helium nuclear wave function. However, the quantum treatment of the full set of nuclear coordinates could be possible within the quasiharmonic approximation [60], which would allow us to decouple the degrees of freedom mostly involving the tritium-helium, while at the same time evaluating the influence of the substrate vibrational dynamics, on them and on the decay spectrum. The anharmonicity analysis can provide the couplings between the degrees of freedom of interest and the others, providing estimates of the correctness of the decoupling assumption and at the same time of the vibrational relaxation times.

However, a stronger assumption we made is about the decoupling of the electronic coordinates from the nuclear ones. We used it in two rather opposite declinations: the adiabatic approximation, used before and long after the decay, assuming total adiabaticity of the electrons with respect to the nuclear motion, and the sudden approximation, assuming on the contrary frozen electronic structure. Between these two extremes, a number of theoretical schemes are currently considered to address the relaxation of electronic dynamics during nuclear motion, especially when the latter involves light elements, where quantum effects are more evident. In addition to the evolution of electronic excited states (e.g., within the time-dependent DFT schemes [61]) one must also consider the coupled nuclear motion, either within a semiclassical scheme [62], or within the path-integral scheme [63], if a full quantum accuracy is required. While the latter is still too computationally heavy to address the system of interest, an interesting approach has recently emerged for a quantum perturbative anharmonic treatment with a limited computational cost [64].

We also point out that, in order to further reduce the theoretical uncertainty on the correct form of the interaction between Helium and graphene, it would be of great relevance to know, experimentally, with which probability the final state corresponds to He, He^+ or He^{++} . Such a study for the decay of tritium on graphene is currently unavailable, although a similar measurement has been performed for the case of molecular tritium [65].

The analysis of the model system also requires some consideration. Here we considered only a few possible loading levels, and with symmetric distributions. In a real system, the situation is rather different. While the loading can be somehow controlled and measured, the local tritium distribution at given loading cannot. On the other hand, our results (and others', too [23,32,34]) indicate that the parameters of the potentials are rather dependent on the local level of loading. Therefore, if one wants to achieve a realistic determination of the parameters of the potential (and in turn of the β -decay spectrum) one should consider the statistical distribution of possible environments of tritium-helium on graphene.

Such a statistically extensive analysis cannot be performed with DFT approaches, and one must rely on a much less computationally expensive, fully classical treatment, using empirical interatomic potentials. While we have previously performed similar preliminary analyses on small graphene flakes [32] or highly disordered nanoporous forms [66] using reactive potentials [67], we will eventually need a study focusing on the actual form of graphene substrate proposed by PTOLEMY. This could be, for example, a specific nanoporous form at very low density and low level of defects [24]. To this aim, the recently proposed neural network potentials [68] reaching the same accuracy as DFT, with limited computational cost, may offer an alternative interesting solution.

More broadly speaking, a satisfactory formulation of the tritium β -decay rate in presence of graphene will have to address a number of points that are still left open by the current analysis. Among these, for example, is the inclusion of long-range electrostatic corrections, due to the interaction between the outgoing electron and the rest of the system. These are known to be rather relevant for the decay of tritium

in vacuum, but their relevance in the present context is for now hard to quantify. It will then be crucial to understand how they distort the spectrum, as they could represent important systematic effects. Moreover, any further refinement of the theoretical predictions should be accompanied by a study of the associated theoretical uncertainties.

All the aspects above will eventually make up the ingredients leading to the determination of the β -electron spectrum, which should be compared with data to constrain the value of the neutrino mass. To this end, it will be crucial to develop the above proposals, and possibly any other that might be relevant, in the most systematic way possible.

In light of all this, it is clear that this work is just an initial milestone we have set to frame the problem, but many others must follow.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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