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2 **Supplementary Information for**

3 **Lazy electrons in graphene: a time-dependent tight-binding study**

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7 **This PDF file includes:**

8 Supplementary text

9 Figs. S1 to S4

10 References for SI reference citations

11 Supporting Information Text

12 Theory and Model

13 **Adiabatic Born-Oppenheimer Approximation.** Here we discuss the Born-Oppenheimer approximation, the adiabatic case, and
14 its application to the time-dependent Hamiltonian $\hat{H}(t)$ constructed previously. For a particular nuclear configuration, the
15 time-independent Schrödinger equation for the molecular wavefunction can be written as

$$16 \quad H(\mathbf{R}, \mathbf{r})\Psi^{(\alpha)}(\mathbf{R}, \mathbf{r}) = E_\alpha \Psi^{(\alpha)}(\mathbf{R}, \mathbf{r}), \quad [1]$$

17 where n indexes the molecular eigenstate, and the Hamiltonian is divided into electronic kinetic, nuclear kinetic, and interaction
18 potential terms $H(\mathbf{R}, \mathbf{r}) = T_{\text{el}}(\mathbf{r}) + T_{\text{nu}}(\{\mathbf{R}\}) + V(\mathbf{R}, \mathbf{r})$. We can separate the molecular wavefunction into electronic and
19 nuclear parts such that

$$20 \quad \Psi^{(\alpha)}(\mathbf{R}, \mathbf{r}) = \sum_{n,m} b_{n,m}^{(\alpha)} \psi_n(\mathbf{R}; \mathbf{r}) \chi_{n,m}(\mathbf{R}), \quad [2]$$

21 where $\psi_n(\mathbf{R}; \mathbf{r})$ is the n -th electronic eigenstate parametrized by the nuclear configuration $\{\mathbf{R}\}$, and $\chi_{n,m}(\mathbf{R})$ is a nuclear
22 wavefunction. Note that no approximation has been used here, the functions $\psi_n(\mathbf{R}; \mathbf{r})$ form an eigenbasis for the electronic
23 degrees of freedom, and they independently satisfy the time-independent Schrödinger equation for the electron kinetic and
24 interaction potential terms:

$$25 \quad (T_e(\mathbf{r}) + V(\mathbf{R}, \mathbf{r}))\psi_n(\mathbf{R}; \mathbf{r}) = E_n(\{\mathbf{R}\})\psi_n(\mathbf{R}; \mathbf{r}). \quad [3]$$

26 We note that the function $E_n(\{\mathbf{R}\})$ maps out an adiabatic potential energy surface for different nuclear configurations $\{\mathbf{R}\}$.
27 There are N potential energy surfaces, where N is the number of atoms per unit cell. Sometimes adjacent potential energy
28 surfaces touch at a *conical intersection*, or they nearly touch at an *avoided crossing*. At these points, the character of the
29 associated wavefunctions are known to change rapidly (1, 2), and this phenomenon will be increasingly important in the
30 time-dependent simulation.

31 Discarding terms that depend on spatial derivatives of the electronic wavefunction, the electronic basis states labeled
32 by n become independent, making n and m “good” quantum numbers. The ABO molecular wavefunction $\Psi^{(\alpha)}(\mathbf{R}, \mathbf{r})$ is
33 labeled $\Psi^{(\alpha)}(\mathbf{R}, \mathbf{r}) \mapsto \Psi^{(n,m)}(\mathbf{R}, \mathbf{r}) = \psi_n(\mathbf{R}; \mathbf{r}) \chi_{n,m}(\mathbf{R})$. We focus on the electronic part $\psi_n(\mathbf{R}; \mathbf{r})$, which, within the ABO
34 approximation, is a stationary state. We write the Hamiltonian operator in the equation 3 as $\hat{H}(t)$, where the matrix elements
35 are given by the tight-binding formulation.

36 Bands fold into the Brillouin zone when a supercell is used for calculating band structure; clustering of the bands is a
37 result of degeneracy breaking due to the inclusion of vibrations in the classical model of the nuclear degrees of freedom. In
38 principle, the supercell size could increase indefinitely—or to the size of the very large sample—causing the bands to fold into
39 an increasingly smaller Brillouin zone. Our results indicate that *adiabatic* electronic states beginning in a cluster decay very
40 quickly, regardless of supercell size. *Diabatic* electronic states beginning in a cluster experience a decaying autocorrelation over
41 the course of several vibrational periods. For graphene, which has many peaks in its density of states (and hence many band
42 clusters regardless of supercell size), the ABO approximation provides an poor picture of electronic time evolution. Rather, all
43 indications are that a diabatic description where the electronic wavefunction changes little as the nuclei move is much superior.

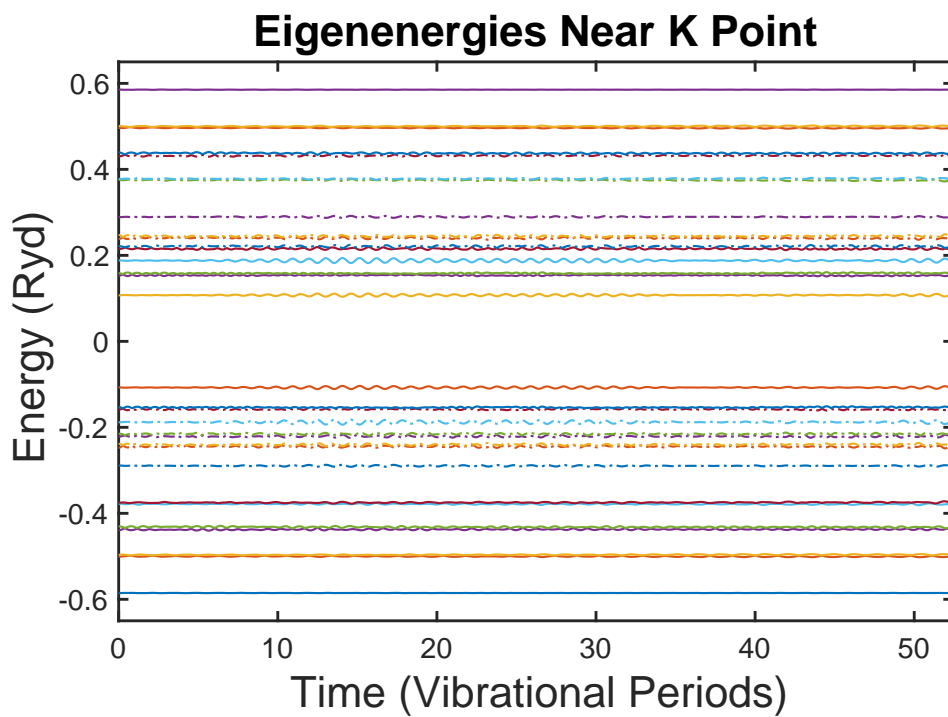


Fig. S1. Time-dependent energy spectrum $E_{\mathbf{k}_e}(t)$ near the K point. On the abscissa, we have plotted time in terms the number of cycles of the shortest vibrational mode, where the shortest vibrational period in our $N = 32$ atom simulation is $190.679 \hbar/\text{Ryd}$.

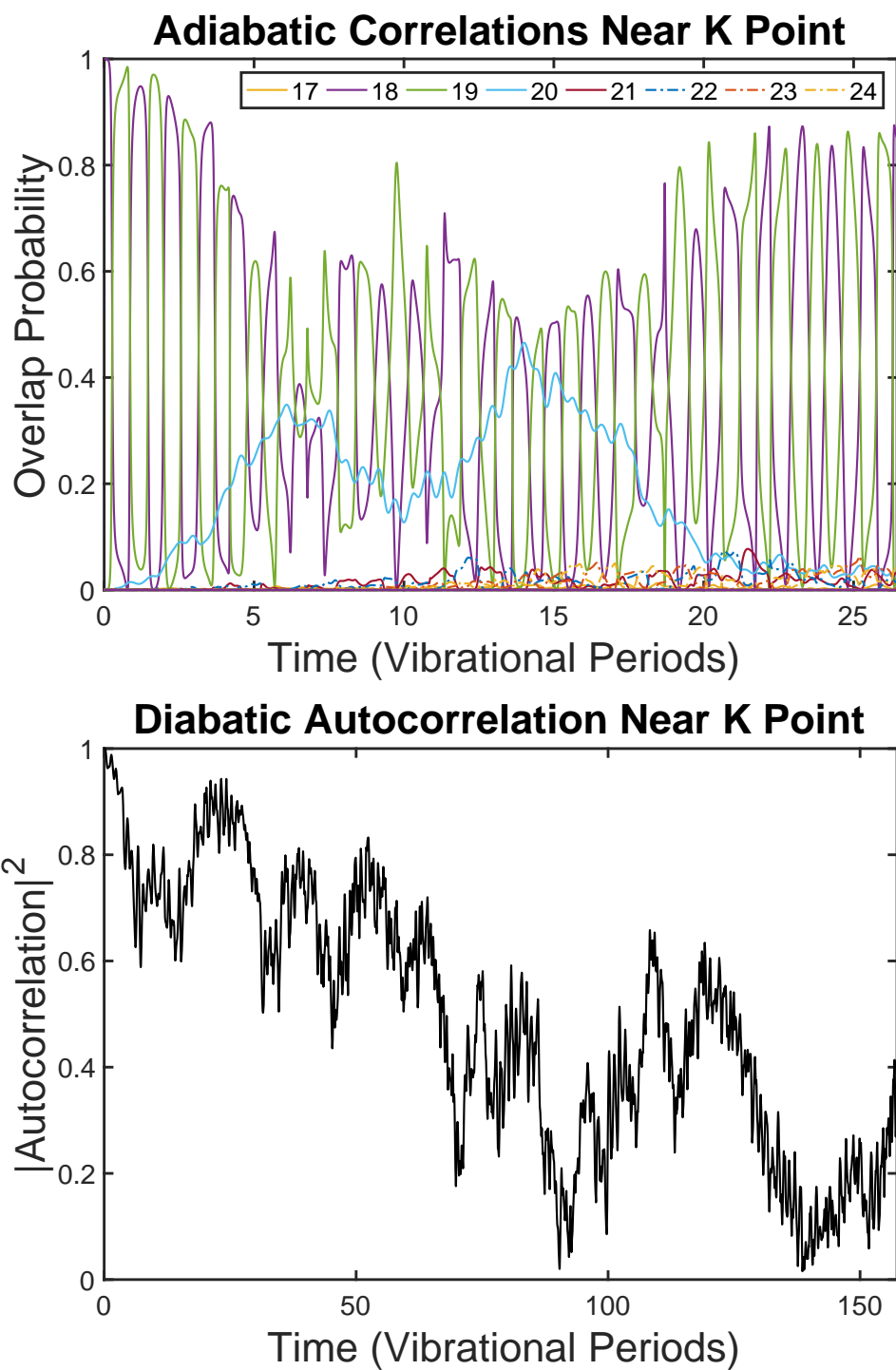


Fig. S2. The overlap probability $P_{k_e}(t)$ (top) and magnitude squared of the autocorrelation $A_{k_e}(t)$ for the electronic state starting in the ABO band $n = 18$, showing the dramatically better persistence of a diabatic-like autocorrelation over an adiabatic one (bottom). Note the six-fold expansion of the time range (abscissa) on the bottom. On the abscissa, we have plotted time in terms the number of cycles of the shortest vibrational mode, where the shortest vibrational period in our $N = 32$ atom simulation is $190.679 \hbar/\text{Ryd}$.

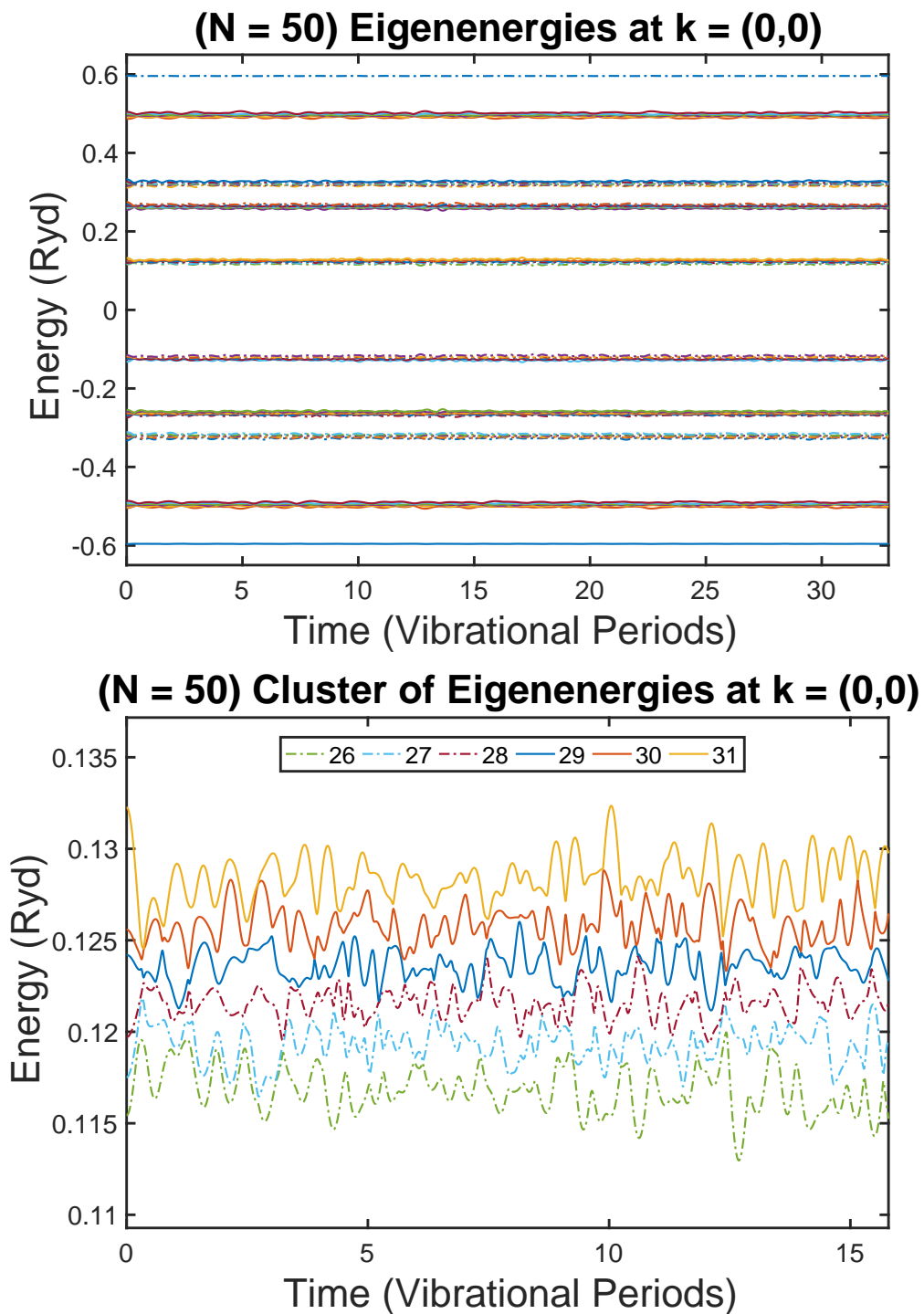


Fig. S3. Time-dependent energy spectrum $E_n(t)$ at the Γ point, where $\mathbf{k} = (0, 0)$: (left) the full spectrum and (right) the cluster containing band $n = 27$. On the abscissa, we have plotted time in terms the number of cycles of the shortest vibrational mode, where the shortest vibrational period in our $N = 50$ atom simulation is $202.755 \hbar/\text{Ryd}$.

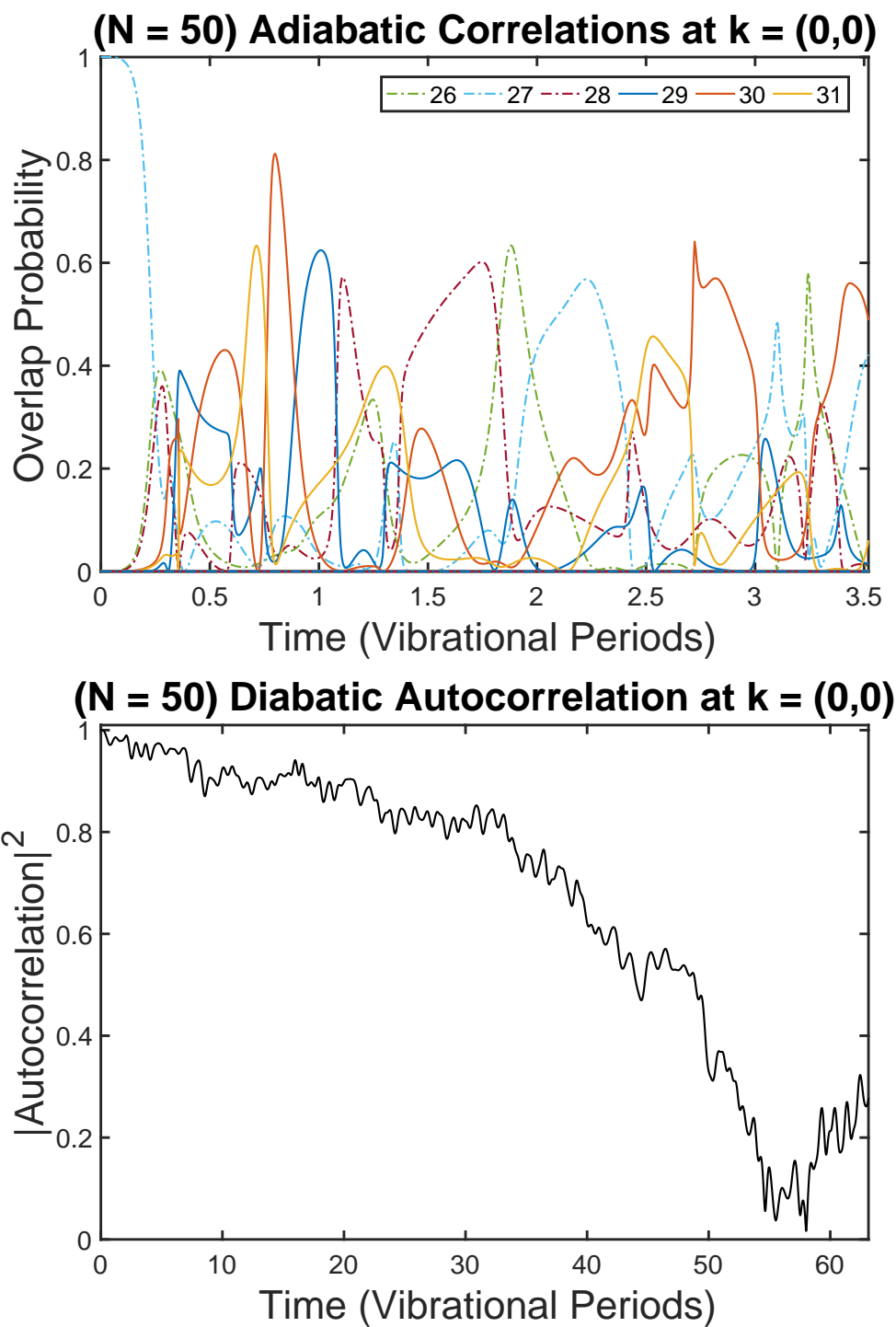


Fig. S4. The overlap probability $P_{\mathbf{k}_e}(t)$ (top) and magnitude squared of the autocorrelation $A_{\mathbf{k}_e}(t)$ for the electronic state starting in the ABO band $n = 27$, showing the dramatically better persistence of a diabatic-like autocorrelation over an adiabatic one (bottom). Note the six-fold expansion of the time range (abscissa) on the bottom. On the abscissa, we have plotted time in terms the number of cycles of the shortest vibrational mode, where the shortest vibrational period in our $N = 50$ atom simulation is $202.755 \hbar/\text{Ryd}$.

44 **References**

- 45 1. Albert J, Hader K, Engel V (2017) Coupled electron-nuclear quantum dynamics through and around a conical intersection.
46 *The Journal of Chemical Physics* 147(6):064302.
- 47 2. Heller EJ (2018) *The semiclassical way to dynamics and spectroscopy*. (Princeton University Press, Princeton, New Jersey).