

# Supporting Information

## Quantum Theory of Electronic Excitation and Sputtering by Transmission Electron Microscopy

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### S1 Invariant matrix element $\mathcal{M}$

As the excitation amplitude in equation (16) contains the invariant matrix element  $\mathcal{M}$  and not  $|\mathcal{M}|^2$ , we are unable to use the spin sum identities typically used to derive many QED cross sections [1, 2]. Nonetheless, the evaluation of  $\mathcal{M}$  in equation (4) is straightforward, though a bit cumbersome. In the Dirac basis [3],

$$\gamma^0 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad \text{and} \quad \gamma^i = \begin{pmatrix} 0 & \sigma^i \\ -\sigma^i & 0 \end{pmatrix}, \quad (\text{S1})$$

where

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad \vec{\sigma} = \left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\}. \quad (\text{S2})$$

The electron spinors in equation (4) can be written as

$$u^1(p) = \sqrt{\epsilon + m} \begin{pmatrix} 1 \\ 0 \\ \frac{p^z}{\epsilon + m} \\ \frac{p^x + ip^y}{\epsilon + m} \end{pmatrix} \quad \text{and} \quad u^2(p) = \sqrt{\epsilon + m} \begin{pmatrix} 0 \\ 1 \\ \frac{p^x - ip^y}{\epsilon + m} \\ \frac{-p^z}{\epsilon + m} \end{pmatrix}, \quad (\text{S3})$$

while

$$\bar{u}^s(p) = u^{s\dagger}(p)\gamma^0. \quad (\text{S4})$$

As justified in the subsection titled *Scattering of free electrons*, we need only evaluate the t-channel contribution to  $\mathcal{M}$  and multiply the result by 2. That is,

$$\mathcal{M}(p_4 p_3 \leftarrow p_2 p_1) \sim e^2 \sum_{s_1, s_2, s_3, s_4} \bar{u}^{s_4}(p_4) \gamma^\mu u^{s_1}(p_1) \left( \frac{1}{p_3 - p_2} \right)^2 \bar{u}^{s_3}(p_3) \gamma_\mu u^{s_2}(p_2). \quad (\text{S5})$$

Substituting equations (S1) through (S4) into (S5) yields  $\mathcal{M}$  in terms of the components of the electrons' 4-momenta. That is,

$$\begin{aligned} \mathcal{M}(p_4 p_3 \leftarrow p_2 p_1) \sim & -\frac{2e^2}{(p_3 - p_2)^2} [(\epsilon_1 + m)(\epsilon_2 + m)(\epsilon_3 + m)(\epsilon_4 + m)]^{-1/2} \\ & \times \left\{ (\epsilon_1 + m)p_4^x [(\epsilon_2 + m)p_3^x + (\epsilon_3 + m)p_2^x] \right. \\ & + 2(\epsilon_1 + m)(\epsilon_3 + m)(p_2^y + ip_2^z)(p_4^y - ip_4^z) \\ & + 2(\epsilon_2 + m)(\epsilon_4 + m)ip_1^z(p_3^y - ip_3^z) \\ & - [(\epsilon_2 + m)(\epsilon_3 + m) + p_2^x p_3^x + (p_2^y + ip_2^z)(p_3^y - ip_3^z)] \\ & \left. \times [(\epsilon_1 + m)(\epsilon_4 + m) + ip_1^z(p_4^y - ip_4^z)] \right\}, \quad (\text{S6}) \end{aligned}$$

where we let  $p_1$  denote the momentum of the beam electron so that  $p_1^x = p_1^y = 0$ . See the Mathematica [4] notebook in the supplemental material for more details.

## S2 Normalization

When integrating over 4-momentum space as is done in the subsection titled , Lorentz invariance constrains a particle's 4-momentum to obey  $p^2 = m^2$ . It follows that the 4-momentum integration measure  $d^4p$  is always multiplied by a delta function  $\delta(p^2 - m^2)$ , i.e.,

$$d^4p \delta(p^2 - m^2) \theta(p^0) = \frac{d^4p}{2p^0} \delta(p_0 - \epsilon_{\mathbf{p}}), \quad (\text{S7})$$

where the Heaviside step function restricts our consideration to particles of positive mass (we note that antiparticles are interpreted as positive mass particles that propagate backwards in time). With this integration measure, the identity operator can be written as

$$\begin{aligned} \hat{I} &= \int \frac{d^4p}{(2\pi)^4} (2\pi) \delta(p^2 - m^2) \theta(p^0) |p\rangle \langle p| \\ &= \int \frac{d^3p}{(2\pi)^3 2\epsilon_{\mathbf{p}}} |p\rangle \langle p| \\ &= \int \frac{d^3p}{(2\pi)^3} |\mathbf{p}\rangle \langle \mathbf{p}|. \end{aligned} \quad (\text{S8})$$

The last equality implies that

$$|p\rangle = (2\epsilon_{\mathbf{p}})^{1/2} |\mathbf{p}\rangle. \quad (\text{S9})$$

### S3 Lab frame $p_3^z$

For the scattering of two free electrons, conservation of 4-momentum allows us to write

$$p_1 + p_2 = p_3 + p_4. \quad (\text{S10})$$

This constrains four of the six components needed to specify the 3-momenta of the two outgoing particles, so that only two components are independent. We choose the independent components to be  $p_3^x$  and  $p_3^y$ . Thus, we wish to find  $p_3^z$  as a function of  $p_1$ ,  $p_2$ ,  $p_3^x$ , and  $p_3^y$ . From this,  $p_4 = p_1 + p_2 - p_3$  is easily obtained, and we have all six components of outgoing 3-momenta needed to calculate the scattering amplitude from equation (16). We start by setting the  $z$ -direction parallel to  $\mathbf{p}_1$ . This means that

$$\begin{aligned} p_4^x &= p_2^x - p_3^x \\ p_4^y &= p_2^y - p_3^y \\ p_4^z &= p_1^z + p_2^z - p_3^z \\ \epsilon_4 &= \epsilon_1 + \Delta\epsilon \end{aligned} \quad (\text{S11})$$

where

$$\epsilon_i = \epsilon_{\mathbf{p}_i} = \sqrt{\mathbf{p}_i^2 + m^2}, \quad \Delta\epsilon = \epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}'}, \quad (\text{S12})$$

and  $\epsilon_{n\mathbf{k}}$  and  $\epsilon_{n'\mathbf{k}'}$  are the eigenvalues of the excited hole and electron states, respectively. We can also write  $\epsilon_1 = \gamma m$  where  $\gamma = 1/\sqrt{1 - \beta^2}$  is the Lorentz factor corresponding to the beam electron's velocity  $\beta$ . Squaring the last line in (S11) and subtracting  $m^2$  then gives

$$\mathbf{p}_4^2 = \mathbf{p}_1^2 + 2\gamma m \Delta\epsilon + \mathcal{O}(\Delta\epsilon^2). \quad (\text{S13})$$

We can ignore terms of order  $\mathcal{O}(\Delta\epsilon^2)$  since  $\Delta\epsilon \ll m$ . Meanwhile, squaring and summing the first three equations in (S11) tells us that

$$\mathbf{p}_4^2 = \mathbf{p}_1^2 + \mathbf{p}_2^2 + \mathbf{p}_3^2 + 2[p_1^z p_2^z - \mathbf{p}_2^\perp \cdot \mathbf{p}_3^\perp - (p_1^z + p_2^z)p_3^z], \quad (\text{S14})$$

where the  $\perp$  superscript denotes the projection perpendicular to  $\hat{z}$ . Subtracting equation (S14) from equation (S13) then yields

$$0 \sim \mathbf{p}_2^2 + \mathbf{p}_3^2 + 2[p_1^z p_2^z - \mathbf{p}_2^\perp \cdot \mathbf{p}_3^\perp - (p_1^z + p_2^z)p_3^z] - 2\gamma m \Delta\epsilon. \quad (\text{S15})$$

Asymptotic formula (S15) can then be solved for  $p_3^z$ , so that

$$p_3^z \sim p_1^z + p_2^z \pm \sqrt{(p_1^z)^2 - (\mathbf{p}_2^\perp - \mathbf{p}_3^\perp)^2 + 2\gamma m \Delta\epsilon}. \quad (\text{S16})$$

We choose the  $-$  from  $\pm$  as we impose that  $\mathbf{p}_3$  is a component of the outgoing crystal electron state, whose  $z$ -momentum is much smaller than that of the beam electron.

## S4 Converging $n_i^{\max}$

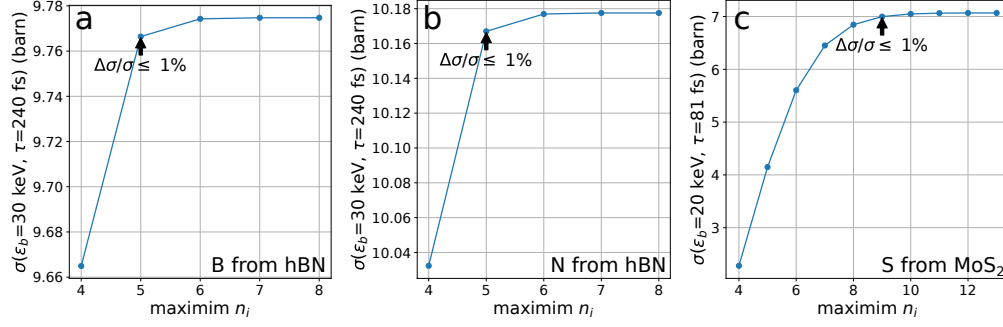


Figure S1: Convergence of the sputtering cross section with respect to the maximum number of beam-induced excitations  $n_i^{\max}$  considered. The simulated beam energies  $\epsilon_b$  are the lowest experimental beam energies used for each material. The excitation lifetimes  $\tau$  are those used to fit the experimental data in figures 5 and 6. Each cross section is deemed converged when any increase in  $n_i^{\max}$  increases the cross section by less than 1%.

## S5 Peaks in the sputtering cross section of hBN



Figure S2: The sputtering cross sections of boron and nitrogen from the hBN armchair edge peak at beam energies much lower than those typically used for microscopy and defect engineering. However, as mentioned in the main text, the validity of our perturbative approximation to the scattering operator breaks down at low beam energies (see *Probability of  $n_i$  excitations*). Thus, the values and positions of these peaks may change if higher order perturbation terms are considered.

## S6 Fitting and converging $S$

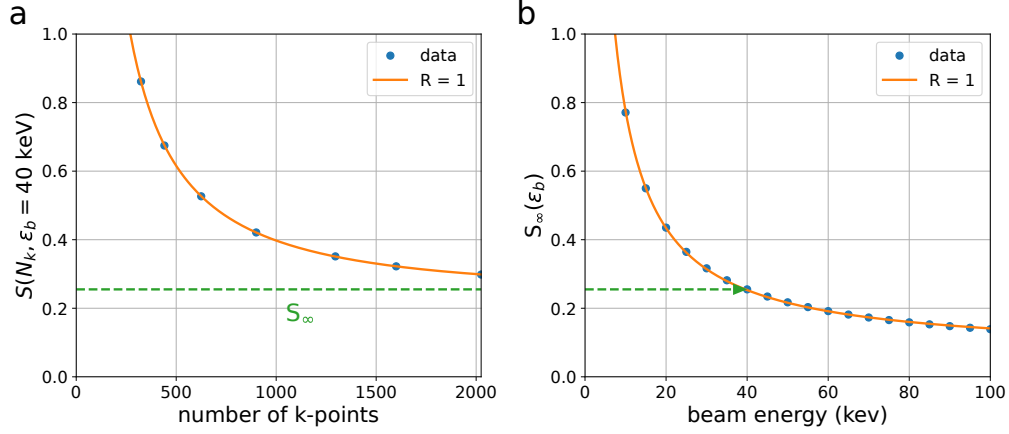


Figure S3: Finding the large crystal limit of  $S(\epsilon_b)$  requires extrapolation. Panel (a) shows the dependence of  $S$  on the number k-points  $N_k$  in the Brillouin zone of hBN under 40 keV irradiation. The simulated points are fitted well by equation (S17). The green dashed line denotes  $S_\infty$ , the asymptotic limit of  $S(N_k)$  for large  $N_k$ . Panel (b) then shows the dependence of  $S_\infty$  on the beam energy  $\epsilon_b$ , which is fitted well by equation (S18). The green arrow in panel (b) illustrates how  $S_\infty(\epsilon_b = 40 \text{ keV})$  is determined by the fit in panel (a).

For a given beam energy  $\epsilon_b$ , we calculate the sum of all transition probabilities  $S$  defined in equation (18) for various k-point densities where the number of k-points in the Brillouin zone is  $N_k$ . We then fit the points to a curve of the form

$$S(N_k, \epsilon_b) = \frac{a}{N_k - b} e^{-cN_k} + S_\infty, \quad (\text{S17})$$

where  $a$ ,  $b$ ,  $c$ , and  $S_\infty$  are all fitting parameters that depend on  $\epsilon_b$  (figure S3a). We repeat this for multiple values of  $\epsilon_b$  ranging from 5 to 100 keV and record the best fit  $S_\infty$  for each  $\epsilon_b$ . Based on the work of Bethe [5–7], we fit the resulting values of  $S_\infty(\epsilon_b)$  to an inverse function,

$$S_\infty(\epsilon_b) = \frac{A}{\epsilon_b - B} + C. \quad (\text{S18})$$

where  $A$ ,  $B$ , and  $C$  are fitting parameters. The parameters for hBN and MoS<sub>2</sub> are given in table S1. The fitted curve can then be substituted for  $S(\epsilon_b)$  in formula (23) to obtain  $P_i(\epsilon_b, n_i)$ , the probability of exciting  $n_i$  electrons in the large crystal limit.

Finally,  $S$  must also be converged with respect all parameters. These include the maximum virtual photon momentum, DFT cutoff energy, and height of the pristine unit cell (figure S4).  $S$  is considered converged with respect to a parameter when any increase in the parameter's precision changes  $S$  by less than 5%.

material	A (eV)	B (eV)	C
hBN	7.655	-0.770	0.06526
MoS <sub>2</sub>	49.05	-3.867	0.3547

Table S1: Fitting parameters of equation (S18) for hBN and MoS<sub>2</sub>.

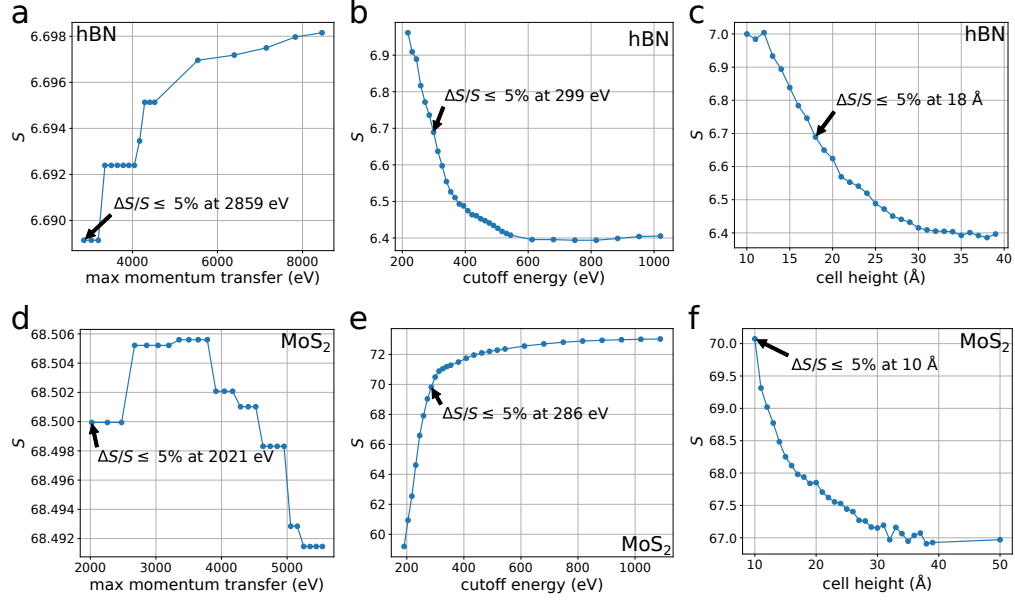


Figure S4: Convergence of  $S$  with respect to the (a and d) maximum magnitude of virtual photon momentum considered, (b and e) plane-wave DFT cutoff energy, and (c and f) height of the unit cell. A  $6 \times 6 \times 1$  k-point mesh and a beam energy of 60 keV is used to generate all six plots. The converged parameters were found to be insensitive to changes in k-point density and beam energy.  $S$  is deemed converged when any increase in precision changes  $S$  by less than 5%.



## S7 Calculating $E_{\min}$

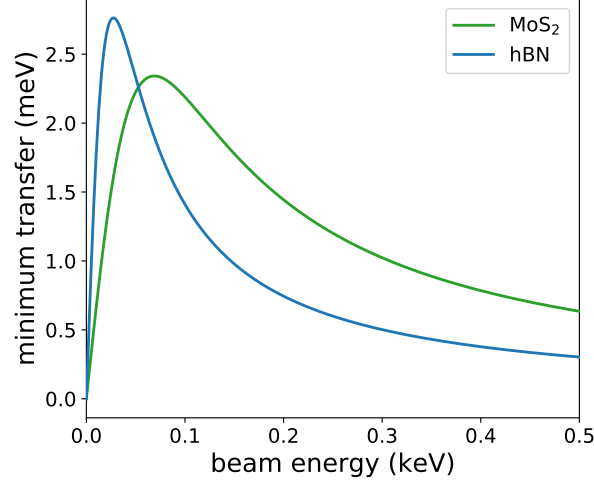


Figure S5: The minimum energy transfer from the beam electron to the target nucleus peaks at very low beam energies and is always much smaller than the nuclei's average thermal kinetic energy of  $\sim 39$  meV at room temperature.

In hBN, a unit cell contains a boron and nitrogen atom. As these atoms have similar masses and displacement thresholds (table 1), the sputtering of both atoms should be considered for a given beam energy. Thus, we approximate the maximum cross sectional area  $\sigma_{\max}$  of these atoms to be  $\Omega_{\text{hBN}}/2$ , where  $\Omega_{\text{hBN}}$  is the area of the hBN unit cell. On the other hand, molybdenum is much heavier than sulfur and has a much larger displacement threshold in MoS<sub>2</sub> [8]. This means that only the sputtering of sulfur needs to be considered. Additionally, of the two sulfur atoms in the MoS<sub>2</sub> unit cell, only the atom on the outgoing surface is eligible to sputter from a pristine system [8]. Therefore,  $\sigma_{\max}$  for sulfur sputtering from MoS<sub>2</sub> is  $\Omega_{\text{MoS}_2}$ , the area of the MoS<sub>2</sub> unit cell.

To approximate  $E_{\min}$ , we use the Rutherford displacement cross section [9–11] as an approximation to equation (2),

$$\sigma_R = \pi \left( \frac{Z\alpha}{|\mathbf{p}|\beta} \right)^2 \left( \frac{E_{\max}}{E_d} - 1 \right). \quad (\text{S19})$$

Setting  $\sigma_R = \sigma_{\max}$  and  $E_d = E_{\min}$  and solving for  $E_{\min}$  yields

$$E_{\min}(\epsilon_b) = E_{\max} \left[ \frac{\Omega}{\pi} \left( \frac{|\mathbf{p}_b|\beta}{Z\alpha} \right)^2 + 1 \right]^{-1}. \quad (\text{S20})$$

Using the Rutherford cross section instead of the McKinley-Feshbach cross section should be accurate for small beam energies for which  $\beta \ll 1$ . This makes it well-suited for finding  $E_{\min}$ , since  $E_d(n_f) < E_{\min}$  only for large  $n_f$ , and large  $n_i$  (and thus  $n_f$ ) are much more likely for small beam energies (figure 3).

With that said, the sputtering cross section is fairly insensitive to the exact value of  $E_{\min}$  when  $E_{\min} \ll E_{\max}$ . This is because the post-collision velocity of the PKA diminishes when the energy transfer  $E$  shrinks. The beam-induced excitations therefore have more time to relax before the PKA reaches the step in the energy surface (see *Effect of excitations on the displacement threshold*). This makes  $P_f$  small for small  $E$ , so that contributions to the integral in equation (3) are extremely tiny for  $E$  near  $E_{\min}$ . As a result, changes in  $E_{\min}$  are essentially immeasurable for beam energies greater than 1 keV. Nonetheless, the use of  $E_{\min}$  is necessary for the calculation of a finite sputtering cross section.

## References

- [1] M. E. Peskin and D. V. Schroeder, *An Introduction to Quantum Field Theory*. Reading, MA: Perseus Books Publishing, L.L.C., first ed., 1995.
- [2] T. Lancaster and S. J. Blundell, *Quantum Field Theory for the Gifted Amateur*. New York, NY, United States of America: Oxford University Press, first ed., 2014.
- [3] J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics*. International series in pure and applied physics, McGraw-Hill, 1964.
- [4] W. R. Inc., “Mathematica, Version 12.3.”
- [5] H. Bethe, “Zur Theorie des Durchgangs schneller Korpuskularstrahlen durch Materie,” *Ann. Phys.*, vol. 397, no. 3, pp. 325–400, 1930.
- [6] T. Susi, J. C. Meyer, and J. Kotakoski, “Quantifying transmission electron microscopy irradiation effects using two-dimensional materials,” *Nat. Rev. Phys.*, vol. 1, pp. 397–405, may 2019.
- [7] S. Kretschmer, T. Lehnert, U. Kaiser, A. V. Krashennnikov, and A. V. Krashennnikov, “Formation of defects in two-dimensional MoS<sub>2</sub> in transmission electron microscope at electron energies below the knock-on threshold : the role of electronic excitations,” *Nano Lett.*, vol. 20, pp. 2865–2870, mar 2020.
- [8] H. P. Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser, and A. V. Krashennnikov, “Two-dimensional transition metal dichalcogenides under electron irradiation: Defect production and doping,” *Phys. Rev. Lett.*, vol. 109, pp. 035503–1–5, jul 2012.
- [9] S. T. Thornton and J. B. Marion, *Classical Dynamics of Particles and Systems*. Boston, MA: Brooks/Cole, 5th ed., 2004.
- [10] J. J. Sakurai and J. Napolitano, *Modern Quantum Mechanics*. San Fransisco, CA: Pearson Education, 2nd ed., 2011.
- [11] A. Yoshimura, M. Lamparski, N. Kharche, and V. Meunier, “First-principles simulation of local response in transition metal dichalcogenides under electron irradiation,” *Nanoscale*, vol. 10, pp. 2388–2397, jan 2018.