Precise predictions and new insights for atomic ionisation from the Migdal effect

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The scattering of neutral particles by an atomic nucleus can lead to electronic ionisation and excitation through a process known as the Migdal effect. We revisit and improve upon previous calculations of the Migdal effect, using the Dirac-Hartree-Fock method to calculate the atomic wavefunctions. Our methods do not rely on the use of the dipole approximation, allowing us to present robust results for higher nuclear recoil velocities than was previously possible. Our calculations provide the theoretical foundations for future measurements of the Migdal effect using neutron sources, and searches for dark matter in direct detection experiments. We show that multiple ionisation must be taken into account in experiments with fast neutrons, and derive the semi-inclusive probability for processes that yield a hard electron above a defined energy threshold. We present results for the noble elements up to and including xenon, as well as carbon, fluorine, silicon and germanium. The transition probabilities from our calculations are publicly available.

I. INTRODUCTION

Despite decades of searching, the precise nature of particle dark matter (DM) remains an enduring mystery. There is a wide-ranging program of direct detection experiments dedicated to measuring the properties of astrophysical DM in terrestrial laboratories [1]. These are based primarily on the possibility that DM scatters and imparts an O(keV) kinetic energy to an atomic nucleus. However, for DM masses less than a few GeV this method loses sensitivity, since the nuclear recoil energy becomes smaller than the experimental energy threshold.

An alternative approach for DM direct detection is to search for electromagnetic signals that may be produced when the DM interacts with the atomic nucleus [2–5]. The possibility that an electron may be emitted from an atom after the sudden perturbation of the nuclear nucleus has been known since the early 1940s [6–9] and has become known as the ‘Migdal effect’ within the DM community [5]. The broader importance of the Migdal effect for direct detection searches has only recently been established in [10, 11], and further studied in [12–23]. Although the production of electromagnetic signals is suppressed relative to the rate of conventional elastic nuclear scattering, there is a window for sub-GeV DM where the nuclear recoil energy falls below threshold while the electromagnetic signal remains observable.1 Several experiments have now exploited this to constrain the sub-GeV DM parameter space [29–36].

Despite the importance of the Migdal effect for DM searches, the emission of an electron after a sudden jolt to the nucleus by an electrically-neutral projectile has not been measured experimentally.2 This has motivated several experimental proposals that aim to systematically study the Migdal effect over a wide range of energies and with different atomic species [46–48]. The proposals follow the standard practice within the DM community of using neutrons as the electrically-neutral proxy for DM and cover a range of neutron energies from 17 keV in Ref. [47], 565 keV in Ref. [46], to 2.5 MeV and 14.7 MeV in the MIGDAL experiment [48].

The characteristic signal of the Migdal effect is a recoiling ion and an ionisation electron emerging from a common vertex. While the use of lower-energy neutrons allows the Migdal effect to be studied in the kinematic regime relevant for DM experiments, it has the disadvantage that the nuclear recoil and ionisation electron cannot be separately resolved, either spatially or energetically; precise modelling of nuclear recoil quenching and the detector response is then required to test the Migdal effect (see e.g., [49, 50]). In contrast, higher-energy neutrons probe a different energy regime from DM experiments, yet offer the possibility of indirectly or directly imaging the Migdal effect: indirectly in high-pressure gas, where the Migdal effect followed by de-excitation of the atom induces a ‘two-cluster’ topology [46]; and directly in low-pressure gas, where nuclear recoil and ionisation electron tracks can be imaged emerging from a common vertex [48].

The qualitatively different scattering regimes for DM and neutron scattering are illustrated in fig. 1. This figure also introduces the dimensionless ratio $v/\alpha$, the magnitude of the nuclear recoil velocity relative to the fine-structure constant multiplied by the speed-of-light (we work in natural units with $\hbar = c = 1$), which will serve

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1 Polarisation (or atomic) bremsstrahlung produces a similar effect [24–28], but its rate is suppressed relative to the Migdal effect [14].

2 The Migdal effect has been measured experimentally in related scenarios where the recoil is due to $\alpha$-decay [37–40] or $\beta$-decay [41–45].

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The purposes of this article are three-fold. Firstly, given the increasing interest in the Migdal effect for DM searches, and given that there is the potential for upcoming experiments to use this effect for DM discovery [51], precise predictions are needed for the low-energy regime probed by DM experiments. The previous state-of-the-art calculations appeared in Ref. [10] and used a relativistic self-consistent mean-field approach with the approximation of a local central potential [52]. We provide two additional, independent calculations of the Migdal effect. The first uses the GRASP [53–55] and RATIP [56] codes to calculate the bound and continuum wavefunctions, respectively. The second uses the BERTHA [57] code, and serves primarily as a cross-check of our results. Both approaches employ the canonical Dirac-Hartree-Fock method, and include the full non-local exchange potential in place of the empirical local potential employed in [10, 52].

Secondly, the calculation of the Migdal effect in Ref. [10] assumed the dipole approximation. While this is a good approximation in the regime \( v \ll \alpha \) characteristic of DM experiments, it is expected to fail at the higher values of \( v/\alpha \) that can be probed in neutron scattering. We therefore calculate the Migdal transition probabilities without making this approximation, instead evaluating the multi-electron matrix elements. Furthermore, we provide a detailed characterisation of the regime of validity of the dipole approximation.

Thirdly, multiple electrons can be ionised through the Migdal effect in the regime where \( v \simeq \alpha \) [58–64], and so we calculate the probability of double ionisation events in neutron-beam experiments, as well as in DM scattering. We also introduce the ‘semi-inclusive’ probability to produce a hard electron in addition to one-or-more soft electrons (which would be below typical experimental thresholds and therefore not observable). We find that this semi-inclusive rate is needed to obtain accurate predictions for high-energy neutron beam experiments; this is due to the importance of multiple ionisation, which causes the semi-inclusive rate to grow with the energy of the recoiling nucleus.

We present results for the noble elements from helium to xenon, as well as for carbon, silicon, germanium and fluorine. The noble elements are widely used in DM scattering experiments, with CYGNUS planning to operate with gaseous He [65, 66], NEWS-G with gaseous He and Ne [67–69], while Darkside [70] and DEAP-3600 [71] operate with liquid Ar, and LZ [72], PANDA-X [73], XENONnT [74], and the proposed XLZD [51, 75] experiment use liquid Xe. The MIGDAL experiment [48] plans to operate with C and F in the form of low-pressure CF\(_4\) gas, as well as CF\(_4\) mixed with other gases including the noble elements, Si, and Ge.\(^3\) The Migdal transition probabilities we have calculated are publicly available [77] for use by the community.

The paper is organised as follows. In Section II we discuss the evaluation of the Migdal matrix element and introduce the semi-inclusive transition probability. In Section III we present our numerical results in the context of select illustrative examples. Section IV applies our results to DM and neutron-scattering experiments, and we conclude in Section V. Several appendices contain details pertinent to our calculations.

\(3\) A number of DM experiments use Si and Ge semiconductor detectors: the relevant formalism for the Migdal effect in semiconductors has been derived in [16, 21, 76].
of the atom at rest. The required matrix element is then given by

$$\langle \Psi_f | \exp \left( i m_e v \cdot \sum_{k=1}^{N} r_k \right) | \Psi_i \rangle,$$  \hspace{1cm} (1)

where \(m_e\) is the electron mass, \(v\) is the nuclear recoil velocity, and the sum is over the position operators \(r_k\) of the \(N\) electrons. The initial and final state electronic wave functions of the atom in the \(v = 0\) frame are denoted by \(\Psi_i\) and \(\Psi_f\) respectively.

Although the above argument relies on the sudden/impulse approximation (the assumption that the projectile-nucleus interaction time scale is short with respect to the electronic response time), the matrix element in eq. (1) holds in general, up to corrections of \(\mathcal{O}(m_e/m_N)\). If the interaction with the nucleus is long range, as in the case of dark matter scattering via a light mediator, then there is an additional form factor \(F(q) \sim 1/q^2\). The situation is more complicated if the projectile interacts with electrons, in which case there will be an atomic form factor \([58]\). While neutrons interact with electrons via a magnetic dipole interaction, this effect is estimated to be negligible \([9, 61]\).

### A. Exclusive transition probability

We first consider the probability to transition to a specific final state, which we term the exclusive transition probability. The matrix element in eq. (1) contains an \(N\)-electron operator. As was pointed out in Ref. \([61]\) in the context of closed-shell atoms, this can be re-written in terms of single-electron matrix elements when the initial and final state wavefunctions are expressed as antisymmetric products of single-electron wavefunctions. We denote the initial and final states by

$$\Psi_i = |\psi_{a_1} \psi_{a_2} \cdots \psi_{a_N}\rangle,$$

$$\Psi_f = |\chi_{b_1} \chi_{b_2} \cdots \chi_{b_N}\rangle,$$  \hspace{1cm} (2)

where \(\{|\psi_{a}\rangle\}\) and \(\{|\chi_{b}\rangle\}\) are two orthonormal bases of four-spinor single-electron wavefunctions from which the initial and final wavefunctions are constructed, respectively. The subscripts \(a_i\) and \(b_i\) denote the set of quantum numbers that describe the wavefunction; for relativistic bound states these are \(n_i\) (\(E\) for continuum states), \(\kappa_i\), and \(m_i\) (see appendix A 1). The transition matrix element for the Migdal effect then simplifies to

$$\langle \Psi_f | e^{i m_e v \cdot \sum r_k} | \Psi_i \rangle = \det(M),$$  \hspace{1cm} (3)

with the \(N \times N\) matrix of single-electron matrix elements

$$M_{\beta \alpha} = \langle \chi_{b_\beta} | e^{i m_e v \cdot r} | \psi_{a_\alpha}\rangle.$$  \hspace{1cm} (4)

Following the standard approach, we evaluate these matrix elements by expanding the exponential operator in spherical tensors, as discussed in detail in appendix A 1.

The exclusive transition probability is then

$$p_v (|\Psi_i\rangle \rightarrow |\Psi_f\rangle) = \det(MM^\dagger).$$  \hspace{1cm} (5)

In practice, the relevant initial state is the atomic ground state, with \(|\psi_{a_\alpha}\rangle\) the occupied orbitals in the ground state. On the other hand, for excitation (ionisation) processes \(|\Psi_f\rangle\) will include one or more excited (continuum) orbitals.

In this section we have, for clarity of presentation, considered the case where the atomic wavefunction can be expressed as a Slater determinant. However, eigenstates of the atomic Hamiltonian are more accurately represented by configuration state functions (CSFs), which are linear combinations of Slater determinants. The generalisation of eq. (3) and eq. (5) to this case is provided in appendix A 2.

### B. Semi-inclusive transition probability

The probability for multiple ionisation becomes significant when the recoil velocity \(v \gtrsim \alpha\), as we shall see in explicit examples in section III. However, for atoms with more than a handful of electrons, the large number of possible final states makes it impractical to calculate all of the exclusive transition probabilities. This motivates us to introduce the semi-inclusive probability \(p_v (|\Psi_i\rangle \rightarrow |\chi_{b_1} X_{\text{soft}}\rangle)\), which includes all final states with an electron in the state \(|\chi_{b_1}\rangle\) and the remaining electrons, denoted collectively by \(X_{\text{soft}}\), in either bound or continuum states with energies below some threshold \(E_{\text{th}}\).

The semi-inclusive rate is of particular relevance for experiments aiming to observe the Migdal effect in neutron scattering. This is because the differential probability falls rapidly with increasing ionisation electron energy; hence, in an experiment where the electron energy threshold is \(E_{\text{th}} \sim \mathcal{O}(\text{keV})\), the expected signal is one hard electron with additional sub-threshold excited or ionisation electrons.

The semi-inclusive transition probability is

$$p_v (|\Psi_i\rangle \rightarrow |\chi_{b_1} X_{\text{soft}}\rangle) =$$

$$\frac{1}{(N-1)!} \sum_{b_2, \ldots, b_N} \left| \langle \chi_{b_1} \cdots \chi_{b_N} | e^{i m_e v \cdot \sum r_k} | \Psi_i \rangle \right|^2,$$  \hspace{1cm} (6)

where the sum is over all states where \(N - 1\) electrons have energy less than \(E_{\text{th}}\) (here and in the following, the sum should be understood to include both the sum over bound orbitals and the integral over continuum orbitals). For \(N > 2\) it is impractical to directly evaluate this expression but, given that the probability of producing multiple electrons above an \(\mathcal{O}(\text{keV})\) threshold is negligible (justified below), a good approximation to the semi-inclusive probability is obtained by replacing \(\sum_{b_2, \ldots, b_N} \rightarrow \sum_{\text{all states}}\). In other words, the semi-inclusive probability is approximately equal to the probability of producing one
hard electron with additional hard or soft electrons, 

\[ p_\text{c}(|\Psi_i\rangle \rightarrow |\chi_{b_1}X_{\text{soft}}\rangle) \approx p_\text{c}(|\Psi_i\rangle \rightarrow |\chi_{b_1}X_{\text{all}}\rangle). \]

This leads to

\[ p_\text{c}(|\Psi_i\rangle \rightarrow |\chi_{b_1}X_{\text{soft}}\rangle) \approx \left\langle \Psi_i \right| e^{-im_e v \cdot \sum r_k} \frac{1}{(N-1)!} \right| \chi_{b_1} \right\rangle \approx \sum_{b_1 \ldots b_N} \left| \langle \chi_{b_1} \ldots \chi_{b_N} \right| e^{im_e v \cdot \sum r_k} \left. \right| \Psi_i \rangle \right|^2, \]

where the final result contains only single-electron matrix elements, with the sum over the occupied orbitals in the initial state. In going from the first to the second line of eq. (7) we have used the orthogonality and completeness of the \(|\chi_{b_1}\rangle\).

In deriving eq. (7), we assumed that the probability of producing multiple electrons above threshold is negligible. We verify this numerically for several atoms in section III, but it is expected to be true in general for sufficiently large \(E_{\text{th}}\). This is because the high-energy continuum radial wavefunctions oscillate rapidly, with wavenumber \(\sim \sqrt{2m_e E_c}\), which suppresses the radial integral with the initial-state bound electrons in the single-electron matrix elements (see eq. (A6)). However, this suppression disappears at high recoil velocities where the spherical Bessel function \(j_L(m_e vr)\) in the integral oscillates with a comparable wavenumber. We therefore expect the approximation in eq. (7) to eventually break down when \(v \gtrsim \sqrt{2E_{\text{th}}/m_e}\) and the probability for multiple hard emission becomes significant. For a typical experimental threshold, this corresponds to \(v/\alpha \gtrsim 8.6\sqrt{(E_{\text{th}}/1\text{ keV})}\), which is larger than the maximum recoil velocity with a D-T neutron source (where the neutron energy is \(\sim 14\text{ MeV}\)) for every element except helium. We have confirmed numerically for helium that this expression provides an excellent estimate for \(\sim\text{keV}\) thresholds.

Note that the above derivation can also be straightforwardly extended to obtain, for example, the two electron semi-inclusive rate \(p(|\Psi_i\rangle \rightarrow |\chi_{b_1}\chi_{b_2}X_{\text{soft}}\rangle)\). However, this is unlikely to be of practical relevance due to the very low probability of producing two high-energy ionisation electrons. The generalisation of eq. (7) to open-shell systems is provided in appendix A 2.

C. Dipole approximation

Most previous works have evaluated the matrix element in eq. (1) using the dipole approximation, where the exponential is expanded to first order in \(v\),

\[ \exp \left( i m_e v \cdot \sum_{k=1}^{N} r_k \right) \approx 1 + i m_e v \cdot \sum_{k=1}^{N} r_k + \ldots \] \hspace{1cm} (8)

Interestingly, the dipole expansion provides a much better approximation to the semi-inclusive rate. This is because the latter depends only on the bound-continuum matrix elements in eq. (7) and, for sufficiently high \(E_{\text{th}}\), inner shell ionisations provide the dominant contribution. The dipole approximation to eq. (7) therefore holds when \(v \ll Z_n/(m_e a_0) = \alpha Z_n\), where \(Z_n\) here denotes the effective nuclear charge for the shell that gives the largest contribution. It is interesting that despite the dipole operator only allowing for single electron transitions, it provides a good approximation to the semi-inclusive probability, including multiple ionisation, up to corrections of order \((v/(\alpha Z_n))^2\).
III. MIGDAL PROBABILITY: NUMERICAL RESULTS AND ILLUSTRATIVE EXAMPLES

The previous section provided a general discussion of the Migdal effect and the methods for calculating transition probabilities when atomic wavefunctions are expressed as anti-symmetric products of single-electron wavefunctions. In this section, we describe our implementations of the general theory, and discuss select examples to illustrate particularly interesting aspects of our results.

We calculate the atomic wavefunctions with two independent implementations of the canonical Dirac-Hartree-Fock (DHF) formalism (for a recent review, see [81]), which use either basis-set or finite-difference methods for the radial functions. The basis-set approach, as implemented in the BERTHA [57] package, is ideally suited for the calculation of integrated probabilities, since the sum over states approaches completeness in a systematic way as the size of the basis set is increased. For the calculation of differential ionisation probabilities we use the GRASP [53–55] and RATIP [56] packages to calculate the bound and continuum wavefunctions, respectively. Further details of our atomic calculations are provided in appendices A 3 and A 4. The use of two completely independent implementations also allows for important cross-checks of our results, and we find excellent agreement between the two approaches. The outputs from our numerical calculations are tables of transition probabilities, which we utilise in the subsequent discussion, and are made available for use by the community [77].

A. Integrated transition probabilities

We begin by discussing the integrated transition probabilities for helium and neon, as plotted in fig. 2 as a function of the nuclear recoil velocity. These atoms cleanly illustrate many of the general features seen in larger atoms. Helium and neon are also of interest as proposed target gases for both the NEWS-G direct DM and MIGDAL neutron-scattering experiments.

In the upper panel of fig. 2, the solid lines show the ground state-to-ground state (green, \(p_v^0\)), single transition (cyan, \(p_v^1\)) and double transition (purple, \(p_v^2\)) probabilities, and their sum (dark blue, \(p_v^{\text{sum}}\)). These include all possible transitions to bound-excited-orbitals or ionised continuum states, integrated over electron energies. For low nuclear recoil velocities, the most probable outcome is that the entire atom recoils, remaining in the electronic ground state; on the other hand, for sufficiently high-velocity recoils the atom is always fully ionised. In the special case of helium, all of the above quantities can be expressed purely in terms of ground-state matrix elements, using the completeness of the single electron wavefunctions and conservation of probability. Our implementations with BERTHA and GRASP/RATIP give near identical results for these matrix elements.

The dotted lines in the fig. 2 upper panel show the probabilities for single ionisation (cyan) and double ionisation (purple) calculated with GRASP/RATIP; the dark blue-dotted line shows the sum of the ionisation probabilities and \(p_v^0\). From the difference between the ionisation-only and single/double transition (solid) curves we see that, in helium, the final states with excited bound electrons contribute at most 20% of the total probability, and are completely negligible at high recoil velocities.

In the lower panel of fig. 2 we show similar results...
for neon. Here, the solid lines were obtained using BERTHA and we include up to triple transitions. The neon calculation illustrates an important general feature for many-electron atoms, which is the significant probability for multiple ionisation with increasing recoil velocity. We have not calculated quadruple and higher transitions, since it is computationally intensive, but it is clear that these become important in neon when $v \gtrsim \alpha$ and $p_v^\text{semi} = p_v^1 + p_v^2 + p_v^3 + p_v^4$ (dark blue curve) falls significantly below one. Ultimately, for nuclear recoil velocities exceeding the orbital velocity of the inner shell electrons we expect the nucleus to effectively leave the entire electron cloud behind, leading to the complete ionisation of the atom. For neon this corresponds to a velocity of $v \gtrsim 10\alpha$ or a recoil energy of around 50 MeV; recalling that the binding energy per nucleon is around 8 MeV for neon, it seems unlikely that the complete ionisation of the atom from the Migdal effect would be achievable in practice.

The fact that $p_v^\text{semi} = 1$ to a high accuracy at low recoil velocities, where quadruple and higher transitions are negligible, provides a strong consistency check of our results. A further cross-check is provided by our two separate implementations, with the lower sub-panel of fig. 2 showing the percentage difference between our two calculations ($P_{\text{GRASP}} / P_{\text{BERTHA}} - 1$). For ground-ground transitions the agreement is nearly perfect, and for single transitions the calculations agree within 2%. For double transitions the agreement has greater dependence on the recoil velocity, but is never worse than 5%. The reason that the GRASP/RATIP calculation yields slightly lower probabilities is that it includes only a subset of the transitions to excited bound states; BERTHA, on the other hand, does not distinguish between bound and continuum states, and the basis-set set we have used is sufficiently large to achieve good convergence.

B. Transition probabilities in the presence of an energy threshold

Although the probability of multiple ionisation increases with the nuclear recoil velocity, the additional final-state electrons would only be observed by experiments with a very low electron energy threshold. The reason for this can be seen in fig. 3, which shows the probabilities for double transitions in carbon (left) and argon (right) that yields either one (dashed purple line) or two (solid purple line) electrons with energies higher than 1 keV. The probability of obtaining two hard electrons is orders of magnitude smaller than having a single hard-electron across the whole range of nuclear recoil velocities, which extend to the maximum velocity induced by D-T neutron scattering. Accordingly, it is unlikely that Migdal events with multiple energetic electrons will be observed in either neutron-beam or DM experiments.

The more relevant quantity for experiments is, therefore, the semi-inclusive probability to produce one ion.

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4 We also compared our results for neon with Ref. [61], finding good agreement for $v/\alpha < 0.8$. At higher recoil velocities, Ref. [61] obtains larger single and double transition probabilities than both of our calculations (which are in close agreement).

5 For neon, we have included orbitals up to $8s, 8p, 6d$; note that the excited bound orbitals from GRASP are also not strictly orthogonal to the continuum states from RATIP, as discussed in appendix A 3.

6 Ionisation by the Migdal effect necessarily leads to atomic deexcitation, which may result in additional electrons through Auger (or Coster-Kronig) emission. For light atoms, the Auger electron will also be sub-keV. See Ref. [48] for further discussion.

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FIG. 3. Semi-inclusive ionisation probabilities with $E_{th} = 1$ keV as a function of nuclear recoil velocity (solid grey). The dashed cyan and purple curves show the contributions from exclusive single and double transitions, respectively. The solid purple line shows the probability for double ionisation with both electron energies above 1 keV. The panels are for carbon (left) and argon (right).
isolation electron above threshold, with additional bound excitations or sub-threshold ionisation electrons. This is shown by the solid grey line in fig. 3 with a threshold of $E_{\text{th}} = 1 \text{ keV}$ for carbon (left) and argon (right). The dashed cyan and purple curves show the contributions to the semi-inclusive probability from single and double transitions, respectively. The semi-inclusive and exclusive single ionisation curves are closely matched at low recoil velocities, but for recoil velocities $v/\alpha \gtrsim 0.3$ double and higher transitions cannot be neglected and eventually dominate.

The upper panel of fig. 4 shows the contributions from individual initial-state orbitals to the single ionisation probability, as a function of the ionisation electron energy $E_e$. Ionisation from the valence shell provides the dominant contribution at low $E_e$, while high-energy electrons are more likely to be ionised from the inner shell. Relativistic effects are small for fluorine, and the $p_{1/2}$ and $p_{3/2}$ curves are the same up to a multiplicity factor of $2/3$.

The middle panel of fig. 4 shows the contributions of transitions from particular pairs of initial-state orbitals to the double ionisation probability. In this panel we focus on the scenario where one ionisation electron is soft and below a threshold of $E_{\text{th}} = 1 \text{ keV}$; we integrate over the energy of the soft electron and show the differential probability as a function of the hard electron’s energy. For clarity, we have combined the $2p_{1/2}$ and $2p_{3/2}$ contributions and use non-relativistic notation. The combination of ionisation from the inner shell together with the valence shell ($1s, 2p$) provides the dominant contribution at these energies. This behaviour is consistent with that observed for single ionisation, where ionisation from the $1s$ and $2p$ subshells dominates for hard and soft electrons, respectively.

Finally, the lower panel of fig. 4 shows the individual contributions to the sum over orbitals in eq. (7) for the semi-inclusive probability. Again, we see that the leading contribution is from the $1s$ matrix element. The qualitative behaviour observed in fig. 4 is the same for all of the atoms we have studied, and does not change significantly with the recoil velocity up to overall normalisation.

C. Validity of the dipole approximation

In fig. 5 we provide some examples that demonstrate the accuracy of the dipole approximation. First, in the upper panel we show the difference between the exclusive single ionisation probability and the dipole approximation, $p_i^\text{dipole}/p_i^\text{single} - 1$. The solid and dashed curves show ionisation from the $1s$ and valence subshells, respectively, of neon (blue) and xenon (red). As discussed in section II C, and contrary to previous expectations in the literature, we see that the dipole approximation fails at roughly the same recoil velocity for both subshells. In fact, it is only the valence subshell that behaves slightly differently and all other subshells closely follow the $1s$ curve. We also see that the dipole approximation breaks down at a lower recoil velocity for xenon than neon. More generally, we find that the dipole approximation provides a good approximation to the exclusive ionisation probability only when $v \ll \alpha Z_{\text{p}}/n^2$, with $n$ the principal quan-
dipole - inc
s
single
100 \left( \frac{p_{\text{inc}}}{p_{\text{dipole}}} - 1 \right) E R = 1 \text{ keV}

\begin{align*}
0 & 0.2 & 0.4 & 0.6 & 0.8 & 10^{-2} & 10^{-1} & 1 & 100 & 100 \left( \frac{p_{\text{inc}}}{p_{\text{dipole}}} - 1 \right) \\
0 & 0.2 & 0.4 & 0.6 & 0.8 & 10^{-2} & 10^{-1} & 1 & 100 & 100 \left( \frac{p_{\text{inc}}}{p_{\text{dipole}}} - 1 \right)
\end{align*}

FIG. 5. Upper panel: Difference between the exclusive single ionisation probabilities and the dipole approximation for the 1s and valence subshells of neon and xenon. Lower panel: Difference between the semi-inclusive ionisation probability and the dipole approximation for various atoms. The open circles denote where \( v = \alpha \).

\begin{align*}
\frac{d^2 R}{d E_R d E_e} &= \frac{\rho_s A^2 \sigma_n}{2 m_\chi \mu_\chi^2 N n, \kappa} |F_N|^2 \sum_{n, \kappa} \frac{d p_v(n \kappa \rightarrow E_e)}{d E_e} g_\chi(v_{\text{min}}),
\end{align*}

where the local DM density is \( \rho_s \approx 0.3 \text{ GeV cm}^{-3} \), \( m_\chi \) is the DM mass, \( A \) the atomic mass number of the target, \( \mu_\chi \) the DM-nucleon reduced mass, \( \sigma_n \) the spin-independent DM-nucleon scattering cross-section at zero-momentum transfer, and for \( F_N \) we use the Helm nuclear form factor [82]. The probability to ionise an electron with initial quantum numbers \((n, \kappa)\) into a final state with kinetic energy \( E_e \) is \( p_v(n \kappa \rightarrow E_e) \). Finally, the standard integral over the DM velocity distribution is

\begin{align*}
g_\chi(v_{\text{min}}) &= \int_{v_{\text{min}}}^{\infty} f_\chi(\vec{v}_\chi + \vec{v}_\text{Earth}) \frac{1}{|\vec{v}_\chi|} d^3 \vec{v}_\chi, \quad (10)
\end{align*}

where \( f_\chi(\vec{v}_\chi) \) is taken to be a truncated Maxwell-Boltzmann distribution and we follow the recommendations in Ref. [83] and set \( v_0 = \sqrt{2} \sigma_v = 238 \text{ km s}^{-1} \) and \( v_{\text{escape}} = 544 \text{ km s}^{-1} \). We neglect the time-dependence of \( \vec{v}_\text{Earth} \), the motion of the Earth with respect to the galactic rest frame [84]. The minimum velocity of DM that can inelastically scatter to produce a nuclear recoil with energy \( E_R \) and an electronic excitation of energy \( E_{\text{EM}} \) is

\begin{align*}
v_{\text{min}} &= \sqrt{\frac{m_N E_R}{2 \mu^2} + \frac{E_{\text{EM}}}{\sqrt{2 m_N E_R}}}, \quad (11)
\end{align*}

where \( m_N \) is the nucleus mass and \( E_{\text{EM}} = E_e + E_{\text{inc}} \), with \( E_{\text{inc}} \) the (positive) binding energy of the electron before emission. Note that since \( v_{\text{min}} \) depends on \((n, \kappa)\) through \( E_{\text{inc}} \), \( g_\chi(v_{\text{min}}) \) should be included in the sum in eq. (9). For multiple ionisation, \( E_{\text{EM}} \) is modified to include the sum of the binding energies of each of the electrons.

In fig. 6 we show the differential DM scattering rate as a function of the total electronic energy, \( E_{\text{EM}} \), for helium, argon and xenon. Results for He, relevant for the
FIG. 6. Differential DM scattering rate (per unit target mass) as a function of the total electronic energy for helium, argon and xenon targets, with a DM-nucleon spin-independent cross-section of $\sigma_n = 10^{-40} \text{ cm}^2$ and a DM mass of 1 GeV. The lower panel shows the difference between our result and the rate obtained using the dipole approximation for $d\sigma_n/dE_{\text{EM}}$ from Ref. [10], $(d\sigma_n/dE_{\text{EM}})_{\text{dipole}}/(d\sigma_n/dE_{\text{EM}}) - 1$. The cyan dashed line shows the rate of double transitions in helium, where we integrated over the energy of the second, soft electron up to 0.1 keV.

CYGNUS and NEWS-G experiments, have not been presented in the literature before. We have assumed a DM mass of 1 GeV and a DM-nucleon scattering cross-section of $10^{-40} \text{ cm}^2$. For argon (xenon), one can clearly identify the thresholds where ionisation from the $n = 2, 1 (n = 3)$ shells becomes kinematically accessible. The dashed line shows the rate of double transitions in helium, including both double ionisation and ionisation with excitation, where the second electron is soft ($E_2 < 0.1 \text{ keV}$). As expected, the double transition rate is highly suppressed due to the low nuclear recoil velocity ($v/\alpha \lesssim 0.1$) induced by the scattering DM.

The dipole approximation is expected to be valid in the kinematic regime relevant for DM scattering. In the bottom sub-panel of fig. 6 we compare (for Ar and Xe) the rate obtained with our transition probabilities to the dipole approximation results of Ref. [10], $(d\sigma_n/dE_{\text{EM}})_{\text{dipole}}/(d\sigma_n/dE_{\text{EM}}) - 1$. We indeed find good agreement between the two calculations, verifying existing DM limits based on the Migdal effect. In fact, the differences are primarily due to the differing calculations of the atomic wavefunctions, rather than the use of the dipole approximation. Specifically, we use the local DHF exchange potential in contrast to the effective central potential approximation employed in Ref. [10]. In fig. 6 we have used the theoretical values for the orbital binding energies in $E_{\text{EM}}$, which differ between the two calculations. This is the source of the larger differences near thresholds. We provide further comparisons of our ionisation probabilities with the dipole results of Ref. [10] in appendix B.

B. Neutron scattering

There are several experimental proposals to test the theory underlying the Migdal effect with neutron sources. These experiments will probe an energy regime above that being exploited by DM experiments, but the systematic study of the Migdal effect in various atomic species will test theoretical predictions of the Migdal effect over a wide energy regime. We focus on the phenomenology relevant to the MIGDAL experiment since it uses the highest energy neutron sources and results in phenomenology that is most distinct from DM scattering – and was one of the key motivations for the present work.

A schematic representation of the MIGDAL experiment is shown in fig. 7. The experiment will operate with intense neutron beams from D-D and D-T fusion generators, which are directed towards an optical time-projection chamber (OTPC) situated 1 metre away for the D-T generator and 0.5 metres away for the D-D generator. The OTPC will be filled with low-pressure gas: initially pure CF$_4$ and later CF$_4$-based mixtures with noble elements or Si- or Ge-compounds. Nuclear and electron recoils within the low-pressure gas result in ionisation tracks. The tell-tale sign of a Migdal event is a nuclear recoil track and an electron ionisation track emerging from a common vertex. The ionisation tracks must be sufficiently long to discriminate between electron and nuclear recoils; at a pressure of 50 Torr, this implies

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7 We ignore the mild dependence of the neutron intensity on the orientation of the generator and assume that the neutrons are emitted isotropically. We use the neutron energies for the generator orientations that will be used by the MIGDAL experiment.
an electron energy threshold of approximately 5 keV and a nuclear recoil threshold of around 150 keV [48].

The rate for neutron-induced Migdal events in a gas-mixture again factorises and can be expressed as

\[
d^{2}R = \phi_{n} \sum_{i} N_{i}^{s} \frac{d\sigma_{i}^{s}}{dE_{R}} \sum_{n} \frac{d\rho_{i}^{s}(n\kappa \rightarrow E_{e})}{dE_{e}},
\]

where \(\phi_{n}\) is the neutron flux, the sum over \(i\) runs over all species in the gas-mixture (e.g. \(i = \{C, F, Ar\}\) in a CF\(_{4}\)-Ar mixture), and \(N_{i}^{s}\), \(\sigma_{i}^{s}\), and \(d\rho_{i}^{s}(n\kappa \rightarrow E_{e})\) are the number of target atoms in the interaction volume, the neutron-nucleus cross-section, and the transition probability for the \(i\)-th atomic species, respectively. The number of target atoms is calculated assuming the gas is at ambient temperature (293.15 K) and the interaction volume is 80 cm\(^{3}\) so that, for instance, CF\(_{4}\) gas at 50 Torr contains \(1.3 \times 10^{20}\) molecules. To calculate \(N_{i}^{s}\), we treat each CF\(_{4}\) molecule as one carbon atom and four fluorine atoms.

An important difference with respect to DM scattering is that the neutron has sufficient energy to excite the nucleus. Immediately after the scattering, the excited nucleus is moving with respect to the electron-cloud and so can still lead to electron emission through the Migdal effect. Therefore, \(\sigma_{i}^{s}\) should include the contributions from all reactions that result in the topology in fig. 7: elastic scattering, inelastic scattering, \((n, 2n)\) reactions and radiative capture reactions, since all produce bare nuclear recoils (i.e. without accompanying charged tracks) and the photon released during de-excitation of the nucleus escapes the low-pressure gas without interacting. Differential and integrated neutron-nucleus cross-sections that we use in this work are given in appendix C.

Treating the molecule as a sum of discrete atomic nuclei should be a very accurate approximation in the context of the neutron-nucleus interaction, since the de Broglie wavelength of the neutron at D-D or D-T energies is \(\sim 10^{-14}\) m, which is orders of magnitude smaller than the C-F bond length. The approximation of using the atomic result for the transition probability, \(d\rho_{i}^{s}(n\kappa \rightarrow E_{e})\), rather than performing a molecular calculation, requires a more careful justification. As a starting point, it has been shown that the general form of the transition matrix element, eq. (1), remains the same for both atoms and molecules (up to corrections of order \(m_{e}/m_{N}\)) [78]. It is also common practice to model the molecular electronic wavefunctions in terms of anti-symmetric products of single-electron wavefunctions (molecular orbitals). Taken together, this implies that the formalism in section II extends to the case of molecules: this particularly applies to the derivation of the semi-inclusive rate where the only assumption made about the soft-electron wavefunctions is that they are orthogonal and complete, which holds for both atoms and molecules.

In the context of the MIGDAL experiment, we expect that the atomic result for the semi-inclusive transition probability will provide a good approximation to the molecular result. This is because the MIGDAL experiment employs an \(O(\text{keV})\) energy threshold, so as fig. 4 demonstrates, the transition probability is dominated by the core (inner-most) electrons. This is important because, after molecular bonding, the core electrons in the CF\(_{4}\) molecule are only slightly modified from their atomic forms. This is evidenced by the experimental values of the binding energies: the 1s binding energy in the fluorine atom is 697 eV [85], while the 1\(t_{2}/1a_{1}\) states in CF\(_{4}\) (the core states equivalent to 1s) have a binding energy of 695 eV [86]. We therefore expect that when the core electrons dominate the scattering rate, which is the case for the MIGDAL experiment, the atomic transition probability will provide a reasonable approximation to the full molecular result. Further work is warranted to quantify the level of agreement but such a study lies beyond the scope of this work.

With the above assumptions, the result for the fluo-
The lower panel shows the percentage difference between the sum of exclusive transitions and the semi-inclusive rate, \((dR/dE_R)_{e-+2e-}/(dR/dE_R)_{s.-inc} - 1\). We find good agreement at the level of a few % or better across the whole nuclear recoil range; \((dR/dE_R)_{e-+2e-}\) slightly underestimates \((dR/dE_R)_{s.-inc}\), with the small difference arising because the excited bound orbitals from GRASP and the continuum states from RATIP are not strictly orthogonal, as discussed in appendix A.3, so the ionisation with excitation rate is slightly underestimated.

In fig. 10, we compare the number of Migdal events induced by a D-D generator (left set of columns) and a D-T generator (right set of columns) in several single-species gas targets. The expected number of events-per-day is listed above the column for each element, assuming a gas pressure of 50 Torr and an experimental setup as in fig. 7. These were obtained by integrating the semi-inclusive rate above an electron energy threshold of 5 keV and a nuclear recoil energy threshold of 150 keV. The only exception is for xenon with the D-D generator where the end-point energy is approximately 75 keV, so we instead integrated over nuclear recoil energies above 50 keV. With both neutron generators, we see that there is the possibility of inducing tens or hundreds of Migdal events over a short data-taking period consisting of a few days.

The cyan columns in fig. 10 show the single ionisation event-rate relative to the semi-inclusive rate. The purple columns show the event-rate from double transitions\(^9\), again relative to the semi-inclusive rate, stacked above the single ionisation contribution. For helium the single plus double transition rate (i.e. the total height of the cyan and purple columns) almost exactly matches the semi-inclusive rate, consistent with fig. 9. However, for all of the other gases it underestimates the semi-inclusive rate. The discrepancy is largest for lighter atoms (helium excluded) and for the D-T generator where the nuclear recoils extend to larger values of \(v/\alpha\).

Finally, the black line in each column of fig. 10 indicates the event-rate obtained using the dipole approximation, relative to the semi-inclusive rate. The general trend is consistent with that shown in fig. 5: the dipole approximation provides a good approximation for the heavier atoms, while for lighter atoms it significantly underestimates the semi-inclusive rate, especially for the larger nuclear recoil energies induced by the D-T generator.

\(^8\) Experimentally, it may be more favourable to operate with helium gas at higher pressure [48], but for ease of comparison with other elements, we present results for 50 Torr.

\(^9\) For all elements except xenon, this includes both double ionisation and ionisation with excitation, with the latter contributing \(\sim 5\%\) to the double transition rate; only double ionisation is included for xenon.
V. CONCLUSIONS

The excitation or emission of an electron after a sudden jolt to the atomic nucleus by an electrically-neutral projectile is known as the Migdal effect. In recent years, the Migdal effect has gained prominence in direct detection searches for sub-GeV DM, and there are now several proposals to measure the effect using neutron sources. The parameter that characterises the probability of electron emission is $\nu/\alpha$, the dimensionless ratio of the nuclear recoil velocity relative to the fine-structure constant multiplied by the speed of light. Previous studies have focused on the regime where $\nu/\alpha \ll 1$, which is most relevant for DM direct detection searches. We have advanced the theory underlying the Migdal effect in the $\nu \sim \alpha$ regime, introducing the semi-inclusive probability that is essential for accurate predictions in fast neutron scattering.

We have undertaken two independent calculations of the Migdal effect, solving the Dirac-Hartree-Fock equations using the finite difference and basis-set methods as implemented in GRASP and BERTHA, respectively. We have calculated electron-transition probabilities for noble elements from helium to xenon, as well as for carbon, silicon, germanium and fluorine. In addition to calculating single ionisation probabilities, which are in good agreement with previous calculations when $\nu/\alpha \ll 1$, we have undertaken calculations of multiple ionisation. We have shown that multiple ionisation dominates when $\nu \sim \alpha$, but that the probability of obtaining multiple electrons with energies above an $O(\text{keV})$ experimental threshold is extremely small. Accordingly, we have emphasised the importance of the semi-inclusive transition probability, which accounts for all processes that yield one hard electron, with any number of additional soft, sub-threshold electrons. We have also clarified the role of the dipole approximation. While this approximation is only formally defined for single transitions, we have found that it, perhaps surprisingly, yields a good estimate of the semi-inclusive probability for all but the lightest atoms.

We have applied our results for the Migdal effect in the context of both DM direct detection and neutron scattering experiments. In the DM case, we found good agreement between our single ionisation calculations and previous results. Furthermore, we confirmed that the double ionisation rate is highly suppressed, owing to the low nuclear recoil velocities involved, and can be safely ignored. We have performed the first calculations of the Migdal effect in DM-helium scattering, which will enable experiments that use this element to increase their sensitivity to sub-GeV DM. For neutron scattering, we focused on the phenomenology relevant to the MIGDAL experiment, which employs D-D and D-T neutron generators. At the nuclear recoil velocities induced by these generators, we have shown that the multiple ionisation rate is significant and cannot be ignored; it is imperative that the semi-inclusive probabilities are used to provide the most accurate description of the Migdal effect.

Our work has been carried out in the context of atomic systems. While we have argued that the atomic calculations should provide a good approximation for the core-electrons in CF$_4$, a molecular gas that will be used in the MIGDAL experiment, work remains to extend the formalism so that it applies to all electrons in the molecular system. Similarly, we have ignored complications due to the electronic band structure in liquid noble elements, relevant for DM direct detection experiments. Further work is warranted to extend the theory to these systems. We hope to address some of these issues in the future.

Data Access Statement: The data supporting the findings reported in this paper are openly available from the GitHub and Zenodo repositories at [77].

ACKNOWLEDGMENTS

PC is supported by the Australian Research Council Discovery Early Career Researcher Award DE210100446. MJD is supported by the Australian Research Council. This work was supported by the Australian Research Council through the ARC Centre of Excellence for Dark Matter Particle Physics, CE200100008. CM is supported by the UKRI’s Science and Technology Facilities Council (awards ST/N004663/1, ST/V001876/1, ST/T000759/1). We are grateful to members of the MIGDAL Collaboration for discussions and particularly thank T. Marley (Imperial) for generating the neutron scattering cross-sections used in this work. For the pur-
pose of open access, the authors have applied a Creative Commons Attribution (CC BY) licence to any Author Accepted Manuscript version arising from this submission.

Appendix A: Atomic Physics elements

1. Relativistic single-electron matrix elements

To evaluate the Migdal transition matrix element, we require single-electron matrix elements of the form

\[
M_{n\kappa m}^{n'\kappa' m'} = \langle n', \kappa', m' | \exp(i m_e \mathbf{v} \cdot \mathbf{r}) | n, \kappa, m \rangle, \tag{A1}
\]

where \( \langle \mathbf{r} | n, \kappa, m \rangle \) is a four-component atomic Dirac spinor that satisfies

\[
\langle \mathbf{r} | h_D | n, \kappa, m \rangle = \langle \mathbf{r} | \mathbf{\alpha} \cdot \mathbf{p} + \beta m_e V(\mathbf{r}) | n, \kappa, m \rangle = E_n \langle \mathbf{r} | n, \kappa, m \rangle, \tag{A2}
\]

with \( n \) denoting the principal quantum number, \( m \) the \( J_z \) quantum number, \( V(\mathbf{r}) \) the potential, and \( \alpha \) and \( \beta \) are the \( 4 \times 4 \) Dirac matrices \([87]\). The quantum number \( \kappa \) is the eigenvalue of the operator \( K = -\mathbf{\sigma} \cdot \mathbf{l} \) and can be written as

\[
\kappa = \begin{cases} 
-(l + 1) & j = l + 1/2 \quad (\kappa < 0) \\
+l & j = l - 1/2 \quad (\kappa > 0),
\end{cases} \tag{A3}
\]

with \( l \) and \( j \) the orbital and total angular momentum quantum numbers respectively. For continuum states the discrete label \( n \) is replaced with the continuous label \( E \). We normalise our continuum spinors with respect to energy, \[ \int dE \langle \Psi_{E', \kappa', m'} | \Psi_{E, \kappa, m} \rangle = \delta(E - E'). \]

The four-component spinors are separable in radial and spin-angular coordinates and can be written as (see e.g. \([88]\))

\[
\langle \mathbf{r} | n, \kappa, m \rangle = \frac{1}{r} \left[ P_{n, \kappa}(r) \chi_{\kappa, m}(\vartheta, \varphi) + i Q_{n, \kappa}(r) \chi_{-\kappa, m}(\vartheta, \varphi) \right], \tag{A4}
\]

where \( P_{n, \kappa}(r) \) and \( Q_{n, \kappa}(r) \) are, respectively, the large and small component radial functions and \( \chi_{\pm\kappa, m}(\vartheta, \varphi) \) are two-component spin-angular functions.

As usual, the operator \( \exp(i m_e \mathbf{v} \cdot \mathbf{r}) \) is written as the spherical tensor expansion

\[
\exp(i m_e \mathbf{v} \cdot \mathbf{r}) = 4\pi \sum_{L,M} i^L j_L(m_e v r) Y^M_L(\hat{\mathbf{v}}) Y^M_L(\hat{r}), \tag{A5}
\]

where \( j_L(x) \) is the spherical Bessel function. The spin-angular parts of the matrix element are independent of \( \text{sgn}(\kappa) \) and \( \text{sgn}(\kappa') \), which allows us to write the matrix element in the form

\[
M_{n\kappa m}^{n'\kappa' m'} = 4\pi \sum_{L,M} i^L \sqrt{2L + 1} Y^M_L(\hat{\mathbf{v}}) d_{M'}^M(j', m'; j, m) \\
\times \int_0^\infty dr j_L(m_e v r) \left[ P_{n, \kappa}(r) P_{n', \kappa'}(r) \right. \\
\left. + Q_{n, \kappa}(r) Q_{n', \kappa'}(r) \right]. \tag{A6}
\]

The angular coefficients can be determined via the Wigner-Eckart theorem and are given by

\[
d_{M}^{M'}(j', m'; j, m) = (-1)^{j' - m' + 1/2} [j, j']^{1/2} \Pi^*(\kappa, \kappa'; L) \\
\times \left( \begin{array}{ccc} j' & L & j \\ -m' & M & m \end{array} \right) \left( \begin{array}{ccc} j' & L & j \\ 1/2 & 0 & -1/2 \end{array} \right), \tag{A7}
\]

where \([j, j'] = (2j + 1)(2j' + 1)\), and \( \Pi^*(\kappa, \kappa'; L) \) implements the even-parity selection rule and is equal to one if \( l + l' + L \) is even and zero otherwise. In practice, the limits on the sum over \( L \) in eq. (A6) are determined by the selection rules of the 3\( j \)-symbols that appear in eq. (A7).

2. Transition probabilities with configuration state functions

As usual, we describe atomic wavefunctions with configuration state functions. These are linear combinations of Slater determinants that, in the relativistic case, are eigenfunctions of energy, the total angular momentum operators, \( \mathbf{J} \) and \( \mathbf{L} \), and parity. In this appendix we generalise the results of section II, which were derived for wavefunctions consisting of a single Slater determinant. We write the initial and final-state atomic wavefunctions as

\[
|\Psi_i\rangle = \sum \gamma_i C_i^{\gamma} |\Psi_i^{\gamma}\rangle, \\
|\Psi_f\rangle = \sum \gamma_f C_f^{\gamma} |\Psi_f^{\gamma}\rangle, \tag{A8}
\]

with \( |\Psi_i^{\gamma}\rangle = |\psi_{a(\gamma)_1} \cdots \psi_{a(\gamma)_N}\rangle \), \( |\Psi_f^{\gamma}\rangle = |\chi_{b(\gamma)_1} \cdots \chi_{b(\gamma)_N}\rangle \) single-Slater-determinant wavefunctions and \( C_i^{\gamma}, C_f^{\gamma} \) constant coefficients.

a. Exclusive transition probability

Using the above expressions for the initial and final state wavefunctions, the generalisation of the exclusive transition probability from eq. (5) is

\[
p_{\text{exc}} (|\Psi_i\rangle \rightarrow |\Psi_f\rangle) = \left| \sum_{\gamma, \gamma'} (C_f^{\gamma})^{*} C_i^{\gamma} \det (M^{\gamma, \gamma'}) \right|^2. \tag{A9}
\]

As in eq. (4), \( M^{\gamma, \gamma'} \) is an \( N \times N \) matrix of single-electron matrix elements

\[
(M^{\gamma, \gamma'})_{\beta \alpha} = \langle \chi_{b(\gamma')_\beta} | \exp(i m_e \mathbf{v} \cdot \mathbf{r}) | \psi_{a(\gamma)_\alpha} \rangle, \tag{A10}
\]

where \( |\psi_{a(\gamma)_\alpha}\rangle \) and \( |\chi_{b(\gamma')_\beta}\rangle \) are occupied orbitals in \( |\Psi_i^{\gamma}\rangle \) and \( |\Psi_f^{\gamma}\rangle \), respectively.
b. Semi-inclusive transition probability

In section II we defined the semi-inclusive transition probability, which includes all final states containing a single continuum electron with $E_e > E_{th}$ and any number of additional sub-threshold excitations. To perform the sum over final states it is more convenient to work in the determinant basis for the final states. The initial-state atomic wavefunction, on the other hand, is given by a particular linear combination of determinants, as in eq. (A8). The semi-inclusive probability can then be written as

$$p_e(\Psi_i \rightarrow \vert \chi_{b_1} X_{soft} \rangle) = \frac{1}{(N - 1)!} \sum_{b_2, \ldots, b_N}^{(E < E_{th})} \left\langle \chi_{b_1} \cdots \chi_{b_N} \left| e^{i m_e \cdot \mathbf{r}} \sum_k r_k \right| \Psi_i \right\rangle^2$$

In the second line we have approximated $\sum_{b_2, \ldots, b_N}^{(E < E_{th})} \rightarrow \sum_{b_2, \ldots, b_N}^{all states}$, as discussed in section II. In going from the second to the third line we have substituted eq. (A8) for the initial-state wavefunction and used the completeness of the $\{ \vert \chi_{b} \rangle \}$. The identity operator that acts on the subspace of the remaining $N - 1$ electrons is denoted by $\mathbb{I}_{(N - 1)}$. The above expression for the semi-inclusive probability can be further simplified in specific instances. One such case is when each of the determinants that make up the initial-state wavefunction differ by two or more orbitals. This occurs for the group 14 (group IV) elements we consider (C, Si, Ge), where the atomic ground state has $J = 0$ and in relativistic $jj$-coupling is a linear combination of valence configurations $(np_1/2)^2$ and $(np_3/2)^2$. In this case, the cross-terms in eq. (A11) vanish and the semi-inclusive probability is

$$p_e(\Psi_i \rightarrow \vert \chi_{b_1} X_{soft} \rangle) \approx$$

$$\sum_{\gamma} \left| C_{i}^\gamma \right|^2 \sum_{\alpha=1}^{N} \left\langle \chi_{b_1} \left| e^{i m_e \mathbf{r}} \right| \psi_{\alpha} \right\rangle^2.$$  \hspace{1cm} (A12)

Finally, for the group 17 and 18 (group VII and VIII) elements the ground state wavefunction is described by a single Slater determinant and the semi-inclusive probability is simply given by eq. (7).

3. Implementation in GRASP & RATIP

This appendix briefly describes our computation of the atomic wavefunctions using the GRASP [53–55] and RATIP [56] packages.

GRASP is an implementation of the multi-configuration Dirac-Hartree-Fock method in which wavefunctions are expressed as a weighted sum of CSFs. The integro-differential DHF equations for the radial functions are solved using finite-difference methods as part of an iterative, self-consistent field procedure. GRASP employs an exponential radial grid; we use the default value for the first grid point, $r_0 = 2.0 \times 10^{-6}/Z$ with $Z$ the atomic number, and a step size in the range $h = 0.006 - 0.008$ depending on the element. The nuclear charge distribution is modelled by the default Fermi distribution. The Breit interaction and vacuum polarisation and self-energy corrections are included in the configuration interaction.

We initially solve for the atomic ground state wavefunction in an optimal level calculation. The radial functions for the excited orbitals are then obtained via an extended optimal level calculation that includes configurations with a single excitation from the valence subshell. This is repeated several times, successively increasing the maximum principal quantum number, $n$, with all radial functions with lower $n$ held fixed. The resulting set of radial functions is then used to construct all excited and ionised states. We therefore do not allow for relaxation of the orbitals; this is consistent with the sudden approximation employed in the derivation of the Migdal matrix element.

For ionised states, the radial functions for the continuum spinors are calculated using RATIP, which is also based on the GRASP implementation of the multi-configuration DHF method. RATIP employs a radial grid that is exponential at small $r$ and transitions to linear at large $r$. We fix the grid parameters to be $r_0 = 2.0 \times 10^{-6}/Z$, $h = 0.006$, and $h_p = 0.0033$. For our maximum electron energy of $E_e = 20$ keV this corresponds to 50 grid points per wavelength at large $r$. The continuum radial functions are each obtained in an optimal level calculation using a configuration with a single excitation from the valence subshell. This set of contin-
uum radial functions is then used to describe all ionised states.

BERTHA enforces orthogonality between the continuum wavefunctions and the occupied ground state orbitals. However, the excited bound orbitals obtained using GRASP and the continuum orbitals from BERTHA are not strictly orthogonal. As a result, the basis of single-electron wavefunctions obtained using GRASP and BERTHA does not approach completeness. This does not impact the single, double, and semi-inclusive ionisation probabilities we are primarily interested in, but does affect the total integrated probabilities (except for helium where the integrated probabilities can be expressed purely in terms of ground-state matrix elements). This is one of the reasons that the alternative basis-set approach of BERTHA provides a valuable cross-check of our results.

To evaluate the transition matrix elements in section II and appendix A, the wavefunctions need to be converted from the CSF basis to the determinant basis, for which we use the CESD component of BERTHA. Finally, our transition probabilities include contributions up to \( L = 10 \) (\( L = 4 \) for xenon double ionisation), which we find is sufficient to achieve good convergence up to the maximum recoil velocity for D-T neutrons. The one exception to this is helium, for which we include up to \( L = 30 \). This results in excellent convergence up to \( v/\alpha \sim 6 \), while from \( v/\alpha = 6 \) to the D-T endpoint at \( v/\alpha \approx 9.6 \) conservation of probability is still maintained at the level of 4\% or better.

### 4. Implementation in BERTHA

In this appendix we briefly describe the use of basis-set methods to compute the atomic wavefunctions and single-electron matrix elements, as implemented in the software package BERTHA [57].

The radial functions are expanded in a finite basis set. A conventional choice is the so-called \( G \)-spinor basis set, which takes the form

\[
f_{i,\kappa}^{L}(r) = N_{i,\kappa}^{L} r^{\ell+1} \exp(-\lambda_{i,\kappa} r^2), \quad \text{A13}
\]

\[
f_{i,\kappa}^{S}(r) = N_{i,\kappa}^{S} \left( \frac{d}{dr} + \frac{\kappa}{r} \right) f_{i,\kappa}^{L}(r), \quad \text{A14}
\]

\[
= N_{i,\kappa}^{S'} \left( (\ell + \kappa + 1) - 2\lambda_{i,\kappa} r^2 \right) r^{\ell} \exp(-\lambda_{i,\kappa} r^2),
\]

where \( N_{i,\kappa}^{L}, N_{i,\kappa}^{S} \) and \( N_{i,\kappa}^{S'} \) are normalisation constants that prove useful in maintaining numerical accuracy in the calculation of matrix elements. The basis set parameters, \( \{\lambda_{i,\kappa}\} \), are chosen following well-established practices that generate accurate bound-state energies and which approach completeness in a systematic fashion.

In this basis, the radial amplitudes are expressed in terms of the basis set by

\[
P_{n,\kappa}(r) = \sum_{i=1}^{N_{\kappa}} c_{n,i,\kappa}^{L} f_{i,\kappa}^{L}(r), \quad \text{A15}
\]

\[
Q_{n,\kappa}(r) = \sum_{i=1}^{N_{\kappa}} c_{n,i,\kappa}^{S} f_{i,\kappa}^{S}(r), \quad \text{A16}
\]

where \( N_{\kappa} \) is the rank of the expansion and \( 2N_{\kappa} \) is the dimension of the matrix representation of the Dirac operator for symmetry-type \( \kappa \). The expansion coefficients are determined by the solution of a generalised matrix eigenvalue equation of the general form

\[
F_{\kappa} c_{n,\kappa} = E_{n,\kappa} S_{\kappa} c_{n,\kappa}. \quad \text{A17}
\]

The matrix \( F_{\kappa} \) is a matrix representation of the Dirac-Hartree-Fock operator, and includes the effects of the Coulomb interactions in the self-consistent field. The matrix \( S_{\kappa} \) is the block-diagonal Gram (or overlap) matrix in the given \( G \)-spinor basis set.

We can express the single-electron matrix elements in eq. (A6) can be expressed in closed form in terms of a single class of radial integral,

\[
I(L, M; \zeta) = \int_{0}^{\infty} r^M j_{L}(m_{e} vr) \exp(-\zeta r^2) \, dr,
\]

\[
= \frac{(m_{e} v)^L}{2^{L+2} \Gamma(L+\frac{M+1}{2})} \frac{\sqrt{\pi} \, \Gamma(M+L+1)}{\Gamma(L+\frac{M+1}{2})} e^{\frac{1}{4} (m_{e} v)^2}
\]

\[
\times \mathcal{M} \left[ \frac{L - M}{2} + 1, \frac{3}{2}; \frac{(m_{e} v)^2}{4 \zeta} \right], \quad \text{A18}
\]

where \( \mathcal{M}[a; b; x] \) is the confluent hypergeometric function and \( \zeta \) is a real, positive parameter derived from the constituent basis set parameters \( \lambda_{i,\kappa} \) and \( \lambda_{j,\kappa'} \). The parameters \( L \) and \( M \) are both odd or even positive integers and satisfy the subsidiary condition that \( M - L \) is an even integer greater than 2, so that the confluent hypergeometric function always takes the form of a polynomial with a finite number of terms. The radial matrix elements are evaluated by taking appropriate linear combinations of the primitive integrals in eq. (A18).

The solution of the DHF equations using \( G \)-spinors is achieved using the computer program BERTHA. For a basis set of rank \( N_{\kappa} \), the solution of equations of the form (A17) generates a set of \( N_{\kappa} \) positive-energy states and \( N_{\kappa} \) negative-energy states for symmetry-type \( \kappa \). The positive-energy states can be further categorised as being bound-states if \( E_{n,\kappa} < mc^2 \), or virtual states if \( E_{n,\kappa} > mc^2 \).

### Appendix B: Comparison with previous calculations

In this appendix we provide a comparison of our results for the differential single ionisation probability, \( dp_{i,\kappa}/dE_{\kappa} \), with the results from Ref. [10]. The dipole approximation
is used in Ref. [10], so we make the comparison at $v = 10^{-4}$ where the dipole approximation provides accurate results.

In fig. 11, the coloured lines in the upper part of each panel show our results for ionisation from each subshell in carbon, fluorine, neon, argon and xenon. The black dashed lines in each panel show the $1/(2\pi)dp_e/dE_e$ values from Ref. [10]. We use a different convention to normalise the continuum spinors, so our differential probability does not require the $2\pi$ factor. Following Ref. [10], we label the states with the non-relativistic quantum numbers $(n, \ell)$. This means that the $p$-state probabilities are the sum of those for the $p_{1/2}$ and $p_{3/2}$ relativistic states, while the $d$-state probabilities are the sum of $d_{3/2}$ and $d_{5/2}$. The lower part of each panel shows $[1/(2\pi)dp_e/dE_e] / [dp_e/dE_e] - 1$ expressed as a percentage.

In general, we find good agreement at the level of about 30% or better across all of the atomic species. Larger departures occur but typically at very low values of the electron energy, $1\text{eV} \lesssim E_e \lesssim 100\text{eV}$, where the precise form of the potential has more of an impact. Some degree of deviation is expected since Ref. [10] employs a relativistic self-consistent mean-field approach with a local central potential, while we use the canonical Dirac-Hartree-Fock method, which includes the full non-local...
Appendix C: Neutron cross-sections

This appendix gives the neutron–nucleus cross-sections used in this work. The numerical values of the cross-sections in table I are from the ENDF/B-VIII.0 library [89]. The values on the left (right) correspond to nominal neutron energies from a D-D (D-T) neutron generator. We have listed cross-sections for elastic scattering, inelastic scattering, \((n,2n)\) reactions and radiative capture processes as all of these processes can give rise to an electron and nuclear recoil track with a common vertex: the signal for which the MIGDAL experiment is searching [48].

Figure 12 shows the combined differential cross-section for all signal-inducing processes as a function of the nuclear recoil energy. The left and right panels show the spectra expected from an incoming neutron with energy 2.47 MeV and 14.7 MeV, respectively, and the curves extend to the end-point recoil energies. The spectra were generated with GEANT4 v10.5.1 (G4NDL 4.5) [90].

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TABLE I. Cross-sections (in mb) for 2.47 MeV and 14.7 MeV neutrons from ENDF/B-VIII.0 [89]. The cross-sections are given for the main isotopes except for neon and xenon, where the abundance of additional isotopes is substantial (≥5%), so weighted averages at natural abundance are used. σ₀ denotes the total cross-section, and the signal-inducing processes (σₚ) include elastic scattering (n, n), inelastic scattering (n, n’), (n, 2n) reactions and radiative capture (n, γ).

| Energy (MeV)   | ²He | ¹²C | ¹⁹F | ⁴⁰Ar | ³⁴Ne | ⁴⁰Ar | ³⁴Ne |
|----------------|-----|-----|-----|------|------|------|------|
| 2.47 MeV       | 3.239 | 1.613 | 3.038 | 2.474 | 5.050 | 5.760 | 2.514 |
| 14.7 MeV       | 3.239 | 1.613 | 2.131 | 2.028 | 4.318 | 4.097 | 3.876 |

† These cross-sections are in the resonance region for ⁴⁰Ar(n,n) and vary rapidly with energy. The average cross-sections over the range from 2.45 MeV to 2.50 MeV are σ₀ = 4.327 mb and 3.594 mb for (n, n). We use the average values in our calculations.

FIG. 12. Differential neutron cross-sections for signal-inducing processes. The left (right) panel shows the spectra generated by a D-D (D-T) generator with neutrons at 2.47 (14.7) MeV. Each curve is drawn to the maximum recoil energy, which decreases for heavier atoms and lower neutron energy.

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