Density functional theory (DFT) is ubiquitous in materials science because it models electron densities and all resultant materials properties with useful accuracy at reasonable computational cost. The theory is exact – the exact functional of the exact density will give the exact energy of the system \[ \text{exact functional} = \text{exact density} \] – however, the exact functional is undefined. Approximating it with functionals that very small volumes of perfect crystal (~ 10^9 times smaller than in X-ray diffraction) can be selected for acquiring CBED patterns. All of these factors contribute to the very high precision and accuracy in electron density measurements for which QCBED is renowned.

In QCBED, an experimental, point spread function (PSF)-corrected CBED pattern is fitted with a theoretically calculated one by refining the parameters to which the diffracted intensities are most sensitive. Recent methods incorporate angular differentiation to remove most of the inelastic signal that impedes matching with an elastic electron scattering theory \[ F_{\text{calc}}(hkl) \approx F_{\text{exp}}(hkl) \] (Fig. 1). This is accurate only if: (i) all bonding-affected structure factors have been refined; (ii) the IAM represents isolated atoms accurately. The crystal potential, \( V(r) \), is essential to the calculation of CBED patterns and its Fourier coefficients (structure factors), \( V_{hkli} \), are exactly interconvertible with those of \( \rho(r) \), i.e. \( F_{hkli} \), by the Mott-Bethe formula \[ F_{hkli} \approx V_{hkli} \].

In CQCBED, an independent atom model (IAM), which ignores interatomic bonding, is used and the refined parameters include the bonding-affected \( V_{hkli} \).

The differences between the CQCBED-measured structure factors and their IAM counterparts constitute a set of difference structure factors which quantify the bonding potential, \( \Delta V(r) \) (Fig. 1). This is accurate only if: (i) all bonding-affected structure factors have been refined; (ii) the IAM represents isolated atoms accurately.

By replacing the IAM with DFT, QCBED-DFT treats the material as an ensemble of bonded atoms, not independent ones. Instead of refining small subsets of structure factors, QCBED-DFT refines DFT model parameters, altering the simulated electron density in real space and therefore changing all structure factors used to calculate CBED patterns (Fig. 2). At present, QCBED-DFT uses Bloch wave code \[ \text{Wien2k} \] for the DFT intensity calculations and calls \[ \text{Wien2k} \] for the DFT-calculated crystal potential as input (see \[ \text{Wien2k} \] for details).
FIG. 1. (color online) Conventional QCBED (CQCBED). A few parameters are adjusted to fit a calculated CBED pattern to an experimental one, including the structure factors, $V_h$, to which the intensities are most sensitive. These form a very small subset of all structure factors, $V_g$, required for a full dynamical electron scattering calculation. The unrefined remainder, $V_m$, are obtained from an IAM, i.e. $V_{IAM}^m$. As the refinement progresses, the modified structure factors which start with IAM values, $V_{IAM}^h$, take on new values, $V_{CQCBED}^h$. The bonding potential is the difference between the CQCBED-refined and IAM potentials, and is equivalent to computing the Fourier sum using the difference structure factors, $\Delta V_h$. Here, the bonding potential in aluminum from [43] has been used as an example of CQCBED.

FIG. 2. (color online) QCBED-DFT. The DFT model parameters are refined which, when adjusted, change the simulated electron density in real space, thereby changing all structure factors, $V_{DFT}^g$, of the crystal potential returned to the electron scattering calculations. By optimizing the fit between the calculated and experimental CBED patterns, the DFT model parameters are refined (see [62] for details). The present example involves antiferromagnetic NiO – a subject of this work.

Instead of testing density functionals by comparing system energies and materials properties, QCBED-DFT interrogates $\rho(r)$ directly because the experimental CBED patterns being matched are a direct consequence of $V(r)$, and thus $\rho(r)$, in the actual material.

While QCBED experimentally constrains DFT parameters, the $V(r)$ calculated by DFT at each iteration of QCBED-DFT represents the material better than an IAM, increasing the accuracy of QCBED. Furthermore, DFT provides the theoretical framework for translating
the QCBED-DFT-optimized electron density into a large suite of materials properties, assuming that the functional and calculation protocols are sufficiently accurate for the material being modelled [2, 63, 69, 72].

Strongly correlated electron systems have challenged DFT [2, 63, 70] and one way of dealing with electron correlations has been to add the Hubbard energy parameter, \( U \), into the exchange-correlation functional [2, 66, 70]. In our investigations of NiO and CeB₆, we used the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [69, 73] in a GGA(PBE) + \( U \) configuration and we refined \( U \). This was done within the augmented plane wave plus local orbitals (APW + lo) regime of Wien2k [69]. For CeB₆, we also refined the positions of the boron atoms because of significant discrepancies in the literature [74, 75]. All experimental details, DFT and QCBED settings within QCBED-DFT, refinement outputs, materials properties and electronic structure morphologies are discussed in [62].

Figure 2 shows a typical example of a QCBED-DFT refinement from the nine that were performed for NiO (see Tables S1-S4 in [62]). All of them involved the refinement of only 8 parameters, including the Hubbard energy, \( U \), to fit 3,026 independent intensities per pattern. The nine CBED patterns came from regions of different specimen thickness ranging from 1,288 Å to 2,001 Å (see Tables S1-S3 in [62]) and were collected with 202.7 ± 0.2 keV electrons incident near <001>. We report a value of \( U = 7.4 \pm 0.6 \) eV for NiO from our QCBED-DFT refinements, with a Hund exchange parameter of \( J = 0.95 \) eV [24, 66, 67]. This result is within the range of \( U = 4.6 \) eV - 8.0 eV reported previously [60, 67, 79, 85].

Figure 3 presents the QCBED-DFT-optimized electronic structure of NiO at \( T = 0 \) K. Figures 3a - 3c show that the valence and bonding electron densities, \( \rho_{val}(r) \) (a) and \( \Delta \rho(r) \) (b) respectively, are insensitive to the opposed magnetic moments of nearest-neighbor nickel atoms whilst the electron spin density, \( s(r) \) (c), distinguishes them very clearly, as expected.

Whilst CQCBED can determine \( \Delta \rho(r) \) accurately (given an accurate IAM), the determination of \( \rho_{val}(r) \) would require an accurate independent ion model. On its own, CQCBED cannot determine \( s(r) \) because CBED is insensitive to electron spin. Revealing \( \rho_{val}(r) \) and \( s(r) \) is a benefit of the theoretical framework provided by DFT in the context of the electron density born out of that same framework. However, in contrast to stand-alone DFT, the electron density in the present case has been refined against experimental CBED patterns which are a direct consequence of the actual \( \rho(r) \) in the real material.

For CeB₆, in addition to refining \( U \), we also refined the boron position parameter, \( x \) (Figs. 4a, b and f) because of significant discrepancies in previously reported values, i.e. \( x = 0.200 \pm 0.002 \) [74, 78] (see Table S5 in [62]).

We analysed 14 CBED patterns with QCBED-DFT, 7 collected with 121.3 ± 0.2 keV electrons incident near <001> and 7 collected with 202.7 ± 0.2 keV electrons incident near <011>. All patterns came from regions of different specimen thickness ranging from 1,186 Å to 1,719 Å (see Tables S6 and S7 in [62]). This experimental variety tests the precision of the results more robustly than repeated measurements under the same conditions.

Our refinements of \( x \) and \( U \) involved two stages with only one parameter refined during each stage in order to assess and mitigate parameter correlations.

In stage one, all 14 CBED patterns were matched by refining only \( x \), while \( U \) was fixed at values from 1 eV to 6 eV in increments of 1 eV. The mean \( x \) obtained from the 7 refinements near each zone axis, \( \bar{x}_{<uvw>} \), is plotted for each fixed value of \( U \), for each of <001> and <011>, in Fig. 4. The independence of \( x \) from \( U \) is evident in all refinements using CBED patterns near <001> whilst they appear to be linearly correlated in the refinements using near <011> data. This is probably due to the
manifestation of $x$ in two non-collinear directions perpendicular to $<001>$ (Fig. 4b) as opposed to just one such appearance perpendicular to $<011>$ (Fig. 4c). Furthermore, all boron atom columns in $<001>$ projections are well separated from cerium columns, whilst this is not the case for $<011>$. As a first estimate of $x$, we used only the results from the $<001>$ data, averaging over $\bar{x}_{<001>}$ for all fixed values of $U$ to get $\bar{x}_{<001>} = 0.19922$.

Stage two involved fixing $x = 0.19922$ and refining $U$ using all 14 CBED patterns. The results are summarized in Fig. 4d and suggest that $U = 3$ eV. We then repeated the refinements of $U$ with $x$ fixed at $\bar{x}_{<001>} (U = 3$ eV$)$, i.e. $x = 0.19925$. The results of this final set of refinements are summarized in Fig. 4e and are not significantly different to the preceding results in Fig. 4d.

We conclude that $x = \bar{x}_{<001>} (U = 3$ eV$) = 0.1992 \pm 0.0003$ and $U = 3.0 \pm 0.6$ eV. This is in agreement with Sato ($x = 0.19923 \pm 0.00006$) [74], Blomberg et al. ($x = 0.1992 \pm 0.0001$) [76] and Streltsov et al. ($x = 0.1995 \pm 0.0003$) [77] for $x$, whilst our refined value of $U$ agrees with the study of Barman et al. [80].

Applying $x = 0.19925$ (Fig. 4e), i.e. $\bar{x}_{<001>} (U = 3$ eV$)$ without rounding) and $U = 3$ eV, the resulting $\Delta \rho(r)$ at $T = 0$ K is shown in Fig. 4f. A more detailed discussion is presented in [62]; however, the key finding is that the boron atoms do not form octahedra by bonding in an octahedral configuration. Instead, they bond in dumbbell pairs coordinated to nearest-neighbor cerium atoms and this is what results in the formation of boron octahedra. It is notable that the B – B dumbbells have bond lengths of 1.65 Å, which are significantly shorter than the edge lengths of the boron octahedra (1.76 Å). Furthermore, there is very strong anti-bonding electron density ($\Delta \rho(r) < 0$) within each boron octahedron.

A priority of quantum crystallography [53] is to arrive at more accurate electron densities, which raises an important question: How can one test the accuracy of a modelled $\rho(r)$? The answer, at least in the context of this work, is in the form of CQCBED (Fig. 4). In CQCBED, discrepancies between the modelled $\rho(r)$ and the actual $\rho(r)$ from which the experimental CBED patterns arise, will cause individual structure factors to change from the modelled values in order to minimize the pattern mismatch. This is how CQCBED with an IAM has been applied to date – to measure changes in structure factors from IAM values due to bonding (Fig. 4). If the IAM in CQCBED were replaced with the true $\rho(r)$, then the refinement of individual structure factors would result in no changes from their modelled values. We used this principle to test the accuracy of the QCBED-DFT-determined $\rho(r)$.

We performed two sets of CQCBED refinements for NiO and CeB$_6$. In the first set, we used the $V(r)$ (and thus $\rho(r)$) resulting from our QCBED-DFT refinements.
Vital structure factors, density structure factors, CQCBED-DFT- and CQCBED-IAM-refined electron densities that are as close to reality in these materials as may be determined from experimental CBED patterns.

The uncertainties in the CQCBED-DFT-refined structure factors are consistently smaller than those of CQCBED-IAM, with improvements in precision as much as three-fold in some cases (see also Table S11 in [62]). Replacing the IAM with a more accurate DFT model is bound to improve the accuracy of the electron scattering calculations within QCBED, yielding more consistent matches of calculated and experimental CBED patterns and therefore, reduced parameter uncertainties.

The demonstrated ability to ascertain the accuracy of modelled electron densities and the ability to refine DFT model parameters using QCBED-DFT points to the possibility of developing parametrized density functionals guided by QCBED-DFT. Matching a 3-dimensional electron density is a more robust constraint than matching energies. Therefore, QCBED-DFT may be useful in searching for the exact density functional.

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