

Atomic Orbitals from Compton Profiles*

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A recently developed method for the least-squares reconstruction of one-particle reduced density matrices from one-particle expectation values has been applied to isotropic Compton profiles of neon from the literature. The resulting densities in momentum and position space are compared with the ones obtained from ab-initio calculations.

Key words: Density matrix; Compton profile; Least-squares fit; Atomic orbitals; Reconstruction.

1. Introduction

In the last two decades, several algorithms for the least-squares fitting of experimental data by functions that are parametrized in terms of the one-particle reduced density matrix (ODM) [1] have been developed [2–6]. Most of them are restricted to an idempotent sub-class of N -representable [7] ODMs, i.e. they describe the system in an independent-particle model, which corresponds to a single Slater determinant as wave function for the system.

We have recently developed a method for the aforementioned ODM reconstructions that works outside this restriction and varies the ODM over the full set of ensemble-representable one-matrices [5]. The application of this method to theoretical model-systems has shown that the inclusion of electron correlation is necessary to reproduce mixed sets of position and momentum density dependent data [8–10]. The experience gained on these systems indicates, on the other hand, that the idempotency condition may well be retained in cases where only data of one kind are used.

Isotropic Compton profiles $J(q)$ are sometimes fit by a linear combination of functions, i.e.

$$J(q) = \sum_i a_i \tau_i(\zeta_i; q), \quad (1)$$

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where τ are functions of q including some nonlinear parameter(s) ζ . Gaussians [11, 12], Lorentzians [13, 14, 12] and hydrogenic Lorentzians [15] have been employed as functional forms of τ . Such fits allow the straightforward evaluation of the isotropic momentum distribution $\pi(p)$, its moments $\langle p^q \rangle$ [16] and more complicated momentum-space quantities such as stopping powers [17]. However, since they do not have the form of an ODM, they do not permit the *direct* calculation of position-space expectation values, except through additional approximations in the framework of density-functional theory [12, 18].

In this paper we report results from the application of our method to the isotropic Compton profile $J(q)$. We have used the example of neon to demonstrate the possibilities and limitations of an inference of information about orbitals from small sets of momentum-space data.

Section 2 gives a general description of the applied method and its parametrization. Section 3 deals with the application to the Compton profile of atomic neon.

2. Methodology

In the following we discuss only spin-free properties of closed-shell singlet systems. The parametrization of the isotropic Compton profile $J(q)$ is therefore in terms of the *spin-traced* ODM. Extensions to systems including spin are straightforward. We only outline

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the method and refer for more details to [8], [9], and [10].

We write the isotropic Compton profile in terms of the ODM by expanding the latter in a basis set $\{\chi\}$:

$$J(q) = \sum_{ii'} P_{ii'} \cdot \frac{1}{2} \int_{|q|}^{\infty} \int_0^{2\pi} \int_0^{\pi} \tilde{\chi}_i^*(\mathbf{p}) \tilde{\chi}_i(\mathbf{p}) p \sin(\theta_p) d\theta_p d\phi_p dp. \quad (2)$$

$P_{ii'}$ are the elements of the ODM in the $\{\chi\}$ -expansion, and the $\tilde{\chi}_i(\mathbf{p})$ are Fourier-transforms of the basis orbitals $\chi_i(\mathbf{r})$.

We may *not* directly use the $P_{ii'}$ as fitting parameters, since the ODM they represent has to fulfil so-called *N-representability* conditions [7]. It has to be Hermitean, normalized and positive-semidefinite with eigenvalues bounded by 0 and 2 [19].

The first condition (Hermiticity) is equivalent to the orthogonality of the eigenfunctions of the ODM, the *natural orbitals* (NOs). We enforce it by applying a *finite* series of *real-orthogonal* transformations to an initial guess, each transformation associated with only one non-linear parameter, a so-called “rotation-angle” [20]. The latter may then be used as parameters in a least-squares fit.

The other conditions (boundaries on eigenvalues) impose restriction on the *occupation numbers* of the NOs, which may consequently be used as additional linear parameters with linear constraints. If they are kept fixed at values of either 0 or 2, the resulting ODM describes the system in the framework of the independent-particle model. Variation to fractional values means the inclusion of electron correlation on a one-particle level [1].

We employ a nested algorithm [10] to determine the set of rotation angles that minimizes

$$\mathcal{S} = \sum_k (J^{\text{exp}}(q_k) - J(q_k))^2 / \sigma_k^2, \quad (3)$$

where $J^{\text{exp}}(q_k)$ is the experimental profile at the momentum-component value q_k , and σ_k is the associated experimental error. The occupation numbers are determined separately for each functional evaluation (equivalent to a linear least-squares fit with linear constraints). The employed method is general and has been applied to test systems, where electron correlation yielded dramatic improvement in the data reproduction [8–10].

In the present application, however, we will restrict ourselves to idempotent ODMs, i.e. to an independent-particle model. As we will see, this is justified by the sufficient flexibility of the model.

Table 1. List of fits performed on the Compton profile of neon.

| Fit no. | No. of par. | Data | Weight | No. of iter. | \mathcal{S} | GOF ^a |
|---------|-------------|----------------------|--------------|--------------|-----------------------|-----------------------|
| 1 | 8 | 21 exp. ^b | $1/\sigma^2$ | 49 | 0.371 | 0.169 |
| 2 | 5 | 21 exp. ^b | $1/\sigma^2$ | 4 | 0.437 | 0.165 |
| 3 | 4 | 21 exp. ^b | $1/\sigma^2$ | 4 | 0.926 | 0.233 |
| 4 | 5 | 21 exp. ^b | 1 | 4 | 3.67×10^{-4} | 4.79×10^{-3} |
| 5 | 4 | 21 CI ^c | 1 | 3 | 1.84×10^{-6} | 3.29×10^{-4} |

^a See text for definition. – ^b Ref. [21]. – ^c Ref. [28].

3. Valence Compton Profile of Neon

In order to apply the described method, we have chosen the atomic valence Compton profile of neon that has been reported by Eisenberger in 1972 [21]. The author subtracted from his experimental X-ray data an energy-dependent hydrogenic core contribution in order to account for limitations of the impulse approximation for K-shell electrons. As a result, the data are normalized to 8 (instead of the full 10) electrons. We have used the AgK α data for the sake of compatibility with earlier fits [11] and because the MoK α valence data have been shown to exhibit an energy dependence [2], i.e. not to fulfil the impulse approximation [16]. As a basis set, we employed the near-Hartree-Fock STO basis of Clementi and Roetti (CR) [23]. The HF canonical 1s-orbital was kept frozen and unoccupied. The NHF density matrix of CR served as the initial guess. No variation of occupation numbers was performed, since the resulting increase of the number of parameters is not supported by the restricted data set.

This setup results in at most 8 variational parameters: 4 rotation angles to mix the 2s-orbital with the virtual orbitals of s-type, 3 rotation angles for the corresponding mixing within the p-set, and a scaling factor to account for deviations in the normalization of the profiles. Since Eisenberger [21] reports only 21 data points between $q = 0$ and $q = 5.0 \hbar/a_0$, linear dependencies are likely to occur, because the system is overparametrized. The data were weighted by $1/\sigma_k^2$, where σ_k is chosen to be the absolute statistical error of the point k , estimated by interpolation of the data given in [21]. It has been assumed that the σ_k are uncorrelated.

Four fits have been performed with varying numbers of vibrational parameters. They are listed in Table 1. No. 1 varies all parameters described above

| | $\langle p^{-2} \rangle$ | $J(0)$ | N | $\langle p \rangle$ | $\langle T \rangle$ | $\langle p^3 \rangle$ | $\langle p^4 \rangle$ |
|------------------------|--------------------------|--------|-------|---------------------|---------------------|-----------------------|-----------------------|
| 1 | 5.393 | 2.565 | 8.208 | 24.02 | 108.0 | 6785 | 4.833×10^5 |
| 2 | 5.378 | 2.565 | 8.031 | 19.36 | 37.39 | 511.3 | 7814 |
| 3 | 5.513 | 2.571 | 8.041 | 19.57 | 38.84 | 548.4 | 8312 |
| 4 | 5.374 | 2.564 | 8.034 | 19.39 | 37.53 | 514.0 | 7848 |
| NHF ^a | 5.365 | 2.548 | 8.000 | 18.97 | 36.01 | 498.3 | 7784 |
| Gaussians ^b | 5.425 | 2.566 | 8.009 | 18.86 | 32.69 | 317.1 | 1996 |

^a Ref. [23]. – ^b Ref. [11].

Table 2. Expectation values of the momentum moments $\langle p^q \rangle$ for different valence wave functions (unscaled). We report the Compton profile at the peak, $J(0) = \langle p^{-1} \rangle / 2$ and the kinetic energy $\langle T \rangle = \langle p^2 \rangle / 2$, rather than the corresponding moments themselves.

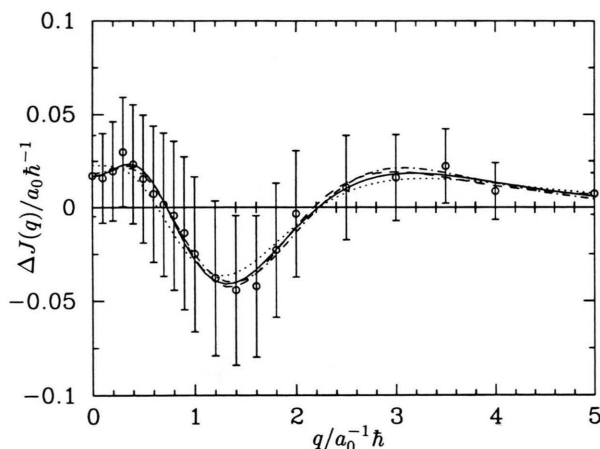


Fig. 1. Difference valence Compton profiles for various fits to the AgK α data of neon [21] (circles with error bars). The reference is the NHF profile [23]. The curves are fits No. 1 (dashed), No. 2 (full), No. 3 (dotted, see Table 1) and a fit by Gaussians (dash-dotted, [11]).

and results in a close reproduction of the experimental data. The parameters are, however, very strongly correlated and consequently undetermined. As a result, the valence momentum-space expectation values derived from the resulting orbitals (see Table 2) are “unreasonable”, especially for the “outer” moments.

In order to avoid this problem, we removed mixing parameters from the s-subset consecutively. If only the mixing-angle between the 2s and the first virtual s-orbital is left, the sum of weighted deviation squares is still comparatively small (No. 2 in Table 1). The reproduction of the Compton profile is surprisingly good, given the fact that only 5 variational parameters (4 angles and the scaling) have been employed (Figure 1). This fit actually exhibits the best “goodness of fit” ($\text{GOF} = \sqrt{\mathcal{S}/(n-m)}$ with n data points and m parameters). Removal of the last s-type mixing angle from the parameter set, however, leads to a serious deterioration of the quality of the fit. For the sake of

completeness, we report the results of this (4 parameter) fit as No. 3.

In order to compare our results with a standard fit to the same data, we have performed another fit of the same type as No. 2, but with equal (unit) weight on the data (No. 4). The results may be compared with the ones obtained by Gadre and Narasimhan [11] with an expansion of the same data [21] into Gaussian functions. However, their fit employs 16 parameters (8 Gaussians with one linear and one non-linear parameter each). Our value for \mathcal{S} is almost the same as the one with the Gaussians (3.70×10^{-4}), despite the fact that only 5 parameters are varied. The reason lies, of course, in the stronger “bias” of our scheme by employing an optimized atomic basis set (Slater-type functions *plus* optimum linear combination).

The quality of data reproduction of the various fits may be judged from Fig. 1, where fit No. 1 (dashed line), No. 2 (full), No. 3 (dotted) and the Gaussian fit (dash-dotted) were used to calculate deviations from the NHF valence Compton profile. Note that fit No. 4 has not been plotted, since it is virtually indistinguishable from fit No. 2. The circles denote the experimental values with error bars of σ_k . It may be seen that with the exception of fit No. 3, all fits reproduce the data with similar quality. No. 3 leaves much to be desired in several regions of the Compton profile, particularly for small q . All fits lie well within the (rather large) error bars.

The p -space valence expectation values (Table 2) of fit No. 4 compared with the results of Gadre and Narasimhan are characterized by a stronger shift towards large p -values and a larger normalization factor (as may be seen from column 3). Consequently, the kinetic energy of our fit is considerably larger than the one obtained from Gaussian fits. This may easily be assigned (see [24]) to the different behaviour of Lorentzian-type functions (which is ultimately the form of our STO functions in momentum space [25]), and Gaussians. Our value tends to overestimate the

| | $\langle p^{-2} \rangle$ | $J(0)$ | N | $\langle p \rangle$ | $\langle T \rangle$ | $\langle p^3 \rangle$ | $\langle p^4 \rangle$ |
|------------------|--------------------------|--------|-------|---------------------|---------------------|-----------------------|-----------------------|
| 2 ^a | 5.472 | 2.735 | 10.00 | 35.51 | 129.8 | 3595 | 9.860×10^4 |
| 5 | 5.555 | 2.739 | 10.00 | 35.23 | 128.7 | 3586 | 9.858×10^4 |
| NHF ^b | 5.480 | 2.728 | 10.00 | 35.20 | 128.5 | 3584 | 9.860×10^4 |
| CI ^c | 5.553 | 2.739 | 10.00 | 35.24 | 128.9 | 3591 | 9.872×10^4 |

^a Valence fit has been rescaled to 8 electrons before adding the NHF [23] core.

^b Ref. [23]. – ^c Ref. [28].

Table 3. Expectation values of the total momentum moments $\langle p^q \rangle$ for different wave functions. We report the Compton profile at the peak, $J(0) = \langle p^{-1} \rangle / 2$ and the kinetic energy $\langle T \rangle = \langle p^2 \rangle / 2$, rather than the corresponding moments themselves.

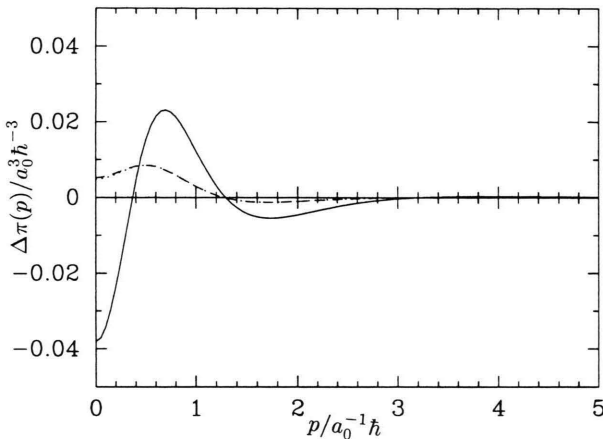


Fig. 2. Difference in the total spherically averaged momentum density $\pi(p)$ for fit No. 2 (full), fit No. 5 (dashed) and CI (dotted, [28]) with respect to the NHF density [23]. The fits are normalized to 10 electrons.

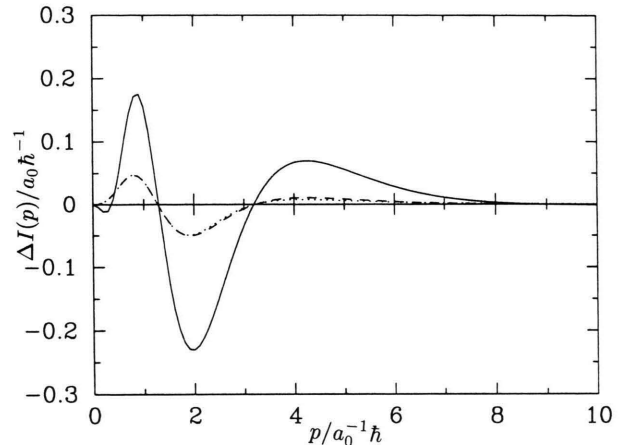


Fig. 3. Difference in the total radial momentum distribution $I(p)$ with respect to the NHF distribution [23]. For the notation and normalization see Fig. 2.

kinetic energy, whereas the Gaussian fit underestimates it. The experimental value lies at $128.94 E_h$ ($E_h = 1$ Hartree = $27.21165 \text{ eV} = 4.359828 \cdot 10^{-18} \text{ J}$) for the total energy [26, 27], calculated by using the virial theorem. By adding the “experimental” valence values to the NHF-core contribution, we obtain 129.93, 130.06 and $125.23 E_h$ for our fits 2 and 4 and for the Gaussian fit, respectively. Note that the value for fit 2 differs somewhat from the one given in Table 3, since it still includes the scale.

In Figs. 2–5 we present difference densities in momentum and position space for three functions with the NHF solution as reference. The full line is fit No. 2 from Table 1 and as such derived from experimental data. The dotted one denotes a CI calculation by Bunge and Esquivel [28] that was done in a basis set consisting of the one of CR [23], enhanced by additional s, p, d, and f-functions. The dashed curve was obtained by a fit (No. 5 in Table 1) to the same set of data points as the experimental ones [21], but using the CI Compton-profile values with unit weight. The parameters varied are the same as in fit 2, but no scale

factor was included. This fit was performed in order to see how close a fit of this type can reproduce values other than the Compton profile.

As one sees, the agreement in momentum space is quite good. The momentum density $\pi(p)$ (Fig. 2) and the radial momentum distribution $I(p)$ (Fig. 3) of fit No. 5 are (on our scale) almost identical with the ones from the CI results. For higher values of p , this agreement will, of course, be poorer (in a relative sense), and higher moments of momentum will deviate more strongly than the lower ones (see Table 3).

As for the position-space properties (which may be calculated directly from N -representable ODMs only), the agreement is much less pronounced. Fit No. 5 gets only tendencies right (Figs. 4 and 5). The near-nucleus region shows the largest deviations, where even the sign of the difference with respect to the NHF result is different (Figure 4). This is in agreement with the fact that high momenta (expressed for example in the $\langle p^4 \rangle$ -value) are not well described by the Compton profile. The electron distribution near the nucleus is strongly affected by the “fast” electrons. The agree-

Table 4. Expectation values of the total position moments $\langle r^q \rangle$ for different wave functions.

| | $\langle r^{-2} \rangle$ | $\langle r^{-1} \rangle$ | $\langle r^1 \rangle$ | $\langle r^2 \rangle$ | $\langle r^3 \rangle$ | $\langle r^4 \rangle$ | $\langle r^{10} \rangle$ | $\langle r^{20} \rangle$ |
|------------------|--------------------------|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|--------------------------|--------------------------|
| 2 ^a | 415.8 | 31.28 | 7.934 | 9.870 | 16.62 | 35.69 | 7.955×10^4 | 1.231×10^{13} |
| 5 | 414.9 | 31.14 | 7.905 | 9.467 | 14.76 | 28.56 | 3.790×10^4 | 5.031×10^{12} |
| NHF ^b | 414.9 | 31.11 | 7.892 | 9.376 | 14.41 | 27.34 | 3.233×10^4 | 4.117×10^{12} |
| CI ^c | 415.0 | 31.11 | 7.935 | 9.545 | 14.94 | 29.01 | 3.880×10^4 | 5.136×10^{12} |

^a Valence fit has been rescaled to 8 electrons before adding the NHF [23] core. – ^b Ref. [23]. – ^c Ref. [28].

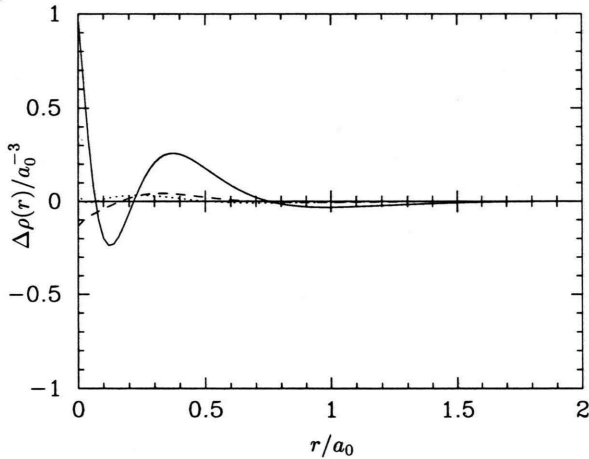


Fig. 4. Difference in the total spherically averaged charge density $\rho(r)$ with respect to the NHF density [23]. For the notation and normalization see Figure 2.

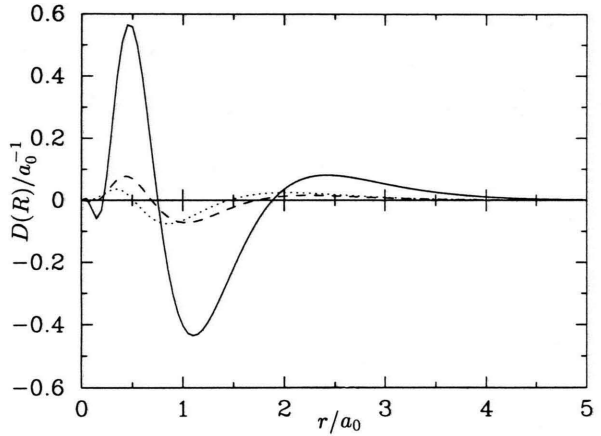


Fig. 5. Difference in the total radial charge density distribution $D(r)$ with respect to the NHF distribution [23]. For the notation and normalization see Figure 2.

ment becomes better for regions of larger r . This may also be seen in Table 4 where the positive powers of r from the CI calculation are reasonably well represented by the fit, whereas the negative ones from the fit are equal to or poorer than the ones from the NHF initial guess.

We note that the differences in the experimental curves occur in both spaces in similar regions as the ones from CI. They are only considerably stronger. Finally, some attention should be paid to the fact that the CI shows a slight enhancement of the momentum density at the origin, whereas the one from experiment is lower than the one obtained from NHF (Figure 2). For both functions, the difference between the $p=0$ value and the local maximum in $\pi(p)$, which leads to *non-monotonic* behaviour [29, 30], is more pronounced than in the Hartree-Fock function. It is interesting to observe, that fits of the form (1) do not always reproduce this feature [11, 12].

4. Conclusions

For the example of the atomic Compton profile of neon we have shown that experimentally obtained one-particle expectation values may be used to obtain an approximate one-particle wave function. The quality of fits obtained in such an *N-representable* ODM framework is comparable to conventional ones, the number of parameters required may be even smaller.

Unlike fitting procedures of form (1), this methodology offers the opportunity to extract information about the structure of the system in the complementary space in general (in contrast to an earlier different approach [31]). However, since the available information is usually insufficient to define the underlying function – the one-particle density matrix – completely, the resulting orbitals are not necessarily unique. This problem, equivalent to the well-known multiple-minima problem in parameter optimization, may be, at

least partly, overcome by a judicious choice of the initial guess and the subspace of parameters allowed to vary. Initial guesses are supplied by *ab-initio* calculations, whereas the parameter space can be restricted by chemical intuition.

In our atomic example, idempotency constraints had to be retained in order to limit the number of parameters. This restriction is not inherent in the applied method, which is general, as pointed out above. Additional restrictions were introduced to avoid strong parameter correlation and resulting "unphysical" behaviour. Given these conditions, we were able to obtain a wave function yielding essentially the experimental Compton profile and reproducing other expectation values quite consistently.

Concerning position space, caution is necessary in the interpretation of the results of our fits. Especially changes (with respect to the HF initial guess) in the small-*r* region are certainly not well described. However, some general tendency (charge density shift from

intermediate to lower and higher radii) may be extracted.

In order to get a firmer grip on the "true" ODM, one has to combine experimental information about both position and momentum space. More recent and considerably more accurate measurements than the one used in this work are available. Applications of our method to molecular and solid-state systems are presently being carried out as well.

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- [31] By employing approximate mapping techniques for *monotonic* momentum densities, it is possible to obtain position space expectation values numerically from Compton profiles. For an example where this has been done see [12].