Application of the $BEf$-scaling approach to electron impact excitation of diopole-allowed electronic states in molecules

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Abstract. We consider the efficacy of the $BEf$-scaling approach, in calculating reliable integral cross sections for electron impact excitation of dipole-allowed electronic states in molecules. We will demonstrate, using specific examples in $H_2$, CO and $H_2O$, that this relatively simple procedure can generate quite accurate integral cross sections which compare well with available experimental data. Finally, we will briefly consider the ramifications of this to atmospheric and other types of modelling studies.

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1. Introduction

Accurate theoretical and experimental integral cross sections for electron impact excitations are available for a number of light and heavy neutral atoms. Through comparisons to such data, the $BEf$-scaling [1] approach was found to convert plane-wave Born (hereafter referred to simply as Born) integral cross sections (ICSs) to reliable cross sections comparable to accurate excitation cross sections at all incident electron energies above threshold. This scaling method provided not only a simple way to calculate excitation cross sections of many atoms, but also to accurately estimate the excitation-autoionisation contributions in many open-shell atoms so that reliable total ionisation cross sections could also be obtained for such atoms [2,3]. If the $BEf$-scaling method was found to also be applicable to molecules, then it would potentially lead to valid excitation and total ionisation cross sections for many molecules, for which more rigorous collision theories might not be currently used because, for instance, of their complex molecular structure. Indeed in view of the paucity of viable theoretical methods to calculate accurate excitation cross sections directly from the Schrödinger equation, even for many simple diatomic molecules, the scaling method discussed later might provide a welcome relief for those who need such cross sections in their applications, e.g., astrophysics, atmospheric physics, materials processing, semiconductor fabrication and combustion modelling.

Validating a scaling method for Born cross sections of molecules requires two initial ingredients:
(i) the Born integral cross sections themselves (or generalised oscillator strengths from which the ICS can be derived),

(ii) reliable experimental or theoretical optical oscillator strengths ($f_o$). Note that this requirement limits the $BEf$-scaling approach to electric-dipole allowed transitions.

In the first case (i) Born cross sections for simple molecules have been calculated since computers became powerful enough to perform such calculations (late 1960s and onwards), but it is now rare to find a paper on Born cross sections for electronic excitations of molecules. This therefore represents a possible impediment in the implementation of the $BEf$-scaling approach. In the second case (ii) Berkowitz [4] has tabulated "f sum rule consistent" optical oscillator strengths for many molecules, including H$_2$, CO and H$_2$O. We now test the success or failure of the $BEf$-scaling procedure by considering its results for some representative molecular-electronic transitions, and respectively comparing those results against relevant reliable experimental ICSs. Specifically, we will do this for the $B_1^{1}\Sigma_u^+\leftarrow X_1^{1}\Sigma_g^+$ transition in H$_2$, the $A_1^{1}\Pi\leftarrow X_1^{1}\Sigma_g^+$ transition in CO and the $\tilde{A}_1B_1^{1}\leftarrow \tilde{X}_1A_1^{1}$ transition in H$_2$O. Note that this comparison will be made in section 3 of this paper. Prior to doing so, however, a brief description of the $BEf$-scaling approach will be outlined in section 2, with conclusions finally being drawn in section 4.

2. Theory

Scaled (plane wave) Born cross sections for dipole-allowed excitations – $f$-scaling and $BE$-scaling – are described in detail in Kim [5], so only the more important points are mentioned here. Note that the Born cross sections are not only subject to the approximations in the collision theory part, but also depend on the accuracy of the wavefunctions used for the initial and final states of the target molecule.

The $f$-scaled Born cross section, $\sigma_f$, is given by:

$$\sigma_f(E_o) = \frac{f_{\text{accur}}}{f_{\text{Born}}} \sigma_{\text{Born}}(E_o)$$

where $E_o$ is the incident electron energy, $f_{\text{accur}}$ is an accurate dipole $f$ value from experiments (e.g. dipole (e,e) or photoabsorption) or from accurate wavefunctions, and $f_{\text{Born}}$ is the dipole $f$ value from the same wavefunctions used to calculate the unscaled Born cross section, $\sigma_{\text{Born}}$. The $f$-scaling process has the effect of replacing the wavefunctions used for $\sigma_{\text{Born}}$ with accurate wavefunctions.

The $BE$-scaled Born cross section, $\sigma_{BE}$, is given by:

$$\sigma_{BE}(E_o) = \frac{E_o}{E_o + B + E} \sigma_{\text{Born}}(E_o)$$

where $B$ is the binding energy of the electron being excited, and $E$ is the excitation energy. The $BE$-scaling corrects the deficiency of the Born approximation at low $E_o$, without losing its well-known validity at high $E_o$.

If an unscaled $\sigma_{\text{Born}}$ is obtained from poor quality wavefunctions while an accurate $f$ value is known, then both $f$-scaling and $BE$-scaling can be applied to obtain a $BEf$-scaled Born cross section, $\sigma_{BEf}$:

$$\sigma_{BEf}(E_o) = \frac{f_{\text{accur}}E_o}{f_{\text{Born}}(E_o + B + E)} \sigma_{\text{Born}}(E_o).$$

We note that it is the $\sigma_{BEf}(E_o)$ integral cross sections that we compare against corresponding experimental values in the next section of this paper.

For the $\sigma_{BEf}(E_o)$ presented in section 3, in H$_2$ we used the $B_1^{1}\Sigma_u^+$ GOSs published by Liu and Hagstrom [6]. Note that their GOSs were a factor of 2 higher than the standard definition
of the GOS [5], because they used excitation energies in Hartrees rather than Rydbergs as the standard definition requires. This was corrected for in the calculation of $\sigma_{\text{Born}}(E_o)$ by Kim [5]. The theoretical $f$ value deduced from the GOS by Liu and Hagstrom [6] was 0.321237, while the sum of the $f$ values adopted by Berkowitz [4] was 0.310594. These values of $f$ ($f_{\text{Born}}$ and $f_{\text{accur}}$ respectively) were used in the $f$-scaling process for $B^1\Sigma_u^+$ in $H_2$. In the case of CO for $A^3\Pi(\nu')$ we chose the theoretical GOSs of Chantranupong et al. [7] to generate $\sigma_{\text{Born}}(E_o)$, while the accurate optical oscillator strengths found in Berkowitz [4] were employed in the $f$-scaling. Finally, in the case of water for $A^1B_1$ excitation, two sets of theoretical GOSs are available in the literature [8,9]. Bhanuprakash et al. [8] calculated their GOS with multiconfiguration wavefunctions, while Durante et al. [9] used wavefunctions from the Random Phase approximation. The $f$ value from the GOS by Bhanuprakash et al. is 0.054 and the $f$ value from the GOS by Durante et al. is 0.046, which is in excellent agreement with that recommended by Berkowitz [4]. Hence, in water we chose the theoretical GOS from Durante et al. to generate $\sigma_{\text{Born}}$ for the $A^1B_1$ electronic state. $BEf$-scaling was then again applied to obtain ICSs that are in principle valid at low and high $E_o$ (see next section).

![ICS: Excitation of the $B^1\Sigma_u^+$ State of $H_2$](image)

**Figure 1.** Integral cross sections ($\times 10^{-16}$ cm$^2$) for electron impact excitation of the $B^1\Sigma_u^+$ state of $H_2$. The $BEf$-scaling result (——) is compared to experimental data from Khakoo and Trajmar [10] (●) and Wrkich et al. (□).
3. Results and Discussion

Considering first the electron impact excitation of the \( B^1\Sigma^+ \) electronic state of \( \text{H}_2 \), we illustrate in Figure 1 the \( BEf \)-scaling ICS results of Kim [5] and the available ICS experimental data from Khakoo and Trajmar [10] and Wrkich \textit{et al.} [11]. Even though the energy range of the measured data is somewhat limited and the number of data points relatively few, it is apparent from Figure 1 that there is, to within the stated measurement uncertainties, quite good agreement between the \( BEf \)-scaling result and the data [10,11]. Note that this latter statement holds for both the shape and magnitude of the ICS, and therefore provides some nice initial evidence for the utility of the \( BEf \)-scaling approach as applied to molecules.

![Figure 1](image1.png)

**Figure 1.** The \( BEf \)-scaling \( ICS \times 10^{-18}\text{cm}^2 \) for electron impact excitation of the \( B^1\Sigma^+ \) state of \( \text{H}_2 \). The \( BEf \)-scaling results [16] (—), unscaled Born results [16] (– – – –) and experimental data from Zobel \textit{et al.} (○), Zetner \textit{et al.} [14] (▼), Lassettre and Skerbele [12] (▲), Zhong \textit{et al.} [15] (■) and Kato \textit{et al.} [16] (●) are shown.

Let us now progress from a homonuclear diatomic (\( \text{H}_2 \)) to a weakly polar heteronuclear diatomic (CO). In this case we also consider each of the vibrationally-resolved \(( \nu' = 0 - 7 \)) sub-levels of the excited electronic \( A^1\Pi \) state in CO. Here there is also more experimental data available [12–16] for comparison and these experimental ICSs range in energy from near-threshold up to 1500 eV. This comparison is made in Figure 2, where we find an excellent level of agreement between the \( BEf \)-scaling result and the measured data [12–16], over the common energy range, for each \( A^1\Pi(\nu') \) vibrational sub-level. Note that the expected inadequacy of the unscaled-Born cross sections is also shown in this figure. The level of agreement seen in Figure 2 between the \( BEf \)-scaled result [16] and the data [12–16] is almost unprecedented in our experience [17], so that Figure 2 provides strong evidence for the applicability of the \( BEf \)-scaling approach in calculating ICSs for dipole-allowed electronic state transitions in molecules. Unfortunately this observation breaks down when resonance effects are present in the scattering process, as was
recently demonstrated by Kawahara et al. [18] for the E^1Π electronic state in CO. Here they found that the BEf-scaling ICS result was in good agreement with the data [13,15,18] away from the resonance, but only in marginal agreement in the region where the resonance was strongest (near-threshold in this case). This work by Kawahara et al. [18] illustrates nicely why the BEf-scaling approach could never hope to supplant ab initio scattering calculations, it simply cannot provide a mechanistic description of the scattering process. Nevertheless where such calculations are impractical or unavailable at this time, we believe the BEf-scaling procedure does offer a very useful alternative.

Finally, in Figure 3, we extend our discussion to the polar triatomic molecule H_2O. Specifically, here we look at the electron impact excitation of its Α^1B_1 electronic state. In this case we compare the BEf-scaling ICS [19] to measured data from Thorn et al. [19] and Lassettre and colleagues [20,21]. As before, it is clear from Figure 3 that, to within the uncertainties in the measurements, there is very good agreement between the BEf-scaling result and the ICS data over the common energy range. Species such as water currently represent a formidable challenge to state-of-the-art scattering calculations, so that it is for molecules like H_2O that we see the BEf-scaling approach finding a really useful niche.

**Figure 3.** Integral cross sections (×10\(^{-16}\)cm\(^2\)) for electron impact excitation of the Α^1B_1 electronic state of H\(_2\)O. The BEf-scaling result (——) is compared to experimental data from Thorn et al. [19] (●) and Lassettre and colleagues [20,21] (□).
4. Conclusions
This short paper has examined the validity of the $BEf$-scaling approach to calculating integral cross sections for dipole-allowed excitations in diatomic and polyatomic molecules. While the $BEf$-scaling approach does not particularly enlighten us as to the fundamental dynamics behind the scattering mechanism in a given system, it does nonetheless appear to predict accurate integral cross sections. This is especially true away from energy regions where resonance phenomena are important. Given that the $BEf$-scaling technique is relatively simple compared to state-of-the-art ab initio theories, we believe it will be valuable for modellers in academia and industry. These modellers require a means of generating reliable cross sections, in order to study the phenomena they are interested in, and we believe the $BEf$-scaling approach provides precisely that.

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References
[1] Kim Y-K 2001 Phys. Rev. A 64, 032713
[2] Kim Y-K and Stone P M 2001 Phys. Rev. A 64 052707
[3] Kim Y-K and Desclaux J P 2002 Phys. Rev. A 66 012708
[4] Berkowitz J 2002 Atomic and Molecular Photoabsorption. Absolute Total Cross Sections (San Diego: Academic Press)
[5] Kim Y-K 2007 J. Chem. Phys. 126 064305
[6] Lin J W and Hagstrom S 1993 Phys. Rev. A 48 166
[7] Chantranupong L, Hirsch G, Bhanuprakash K, Benuker R J, Kimura M and Dillon M A 1992 Chem. Phys. 164 183
[8] Bhanuprakash K, Chandra P, Chabalowski C and Benuker R J 1989 Chem. Phys. 138 215
[9] Durante N, Lamanna U T, Arrighini G P and Buiolotti C 1995 Theor. Chim. Acta 90 115
[10] Khakoo M A and Trajmar S 1986 Phys. Rev. A 34 146
[11] Wrikich J, Mathews D, Kanik I, Trajmar S and Khakoo M A 2002 J. Phys. B 35 4695
[12] Lassettre E N and Skerbele A 1971 J. Chem. Phys. 54 1597
[13] Zobel J, Mayer U, Jung K and Ehrhardt H 1996 J. Phys. B 29 813
[14] Zetner P, Kanik I and Trajmar S 1998 J. Phys. B 31 2395
[15] Zhong Z P, Feng R F, Xu K Z, Zhu L F, Zhang J, Ji Q and Shi Q C 1997 Phys Rev. A 55 1799
[16] Kato H, Kawahara H, Hoshino M, Tanaka H, Brungery M J and Kim Y-K 2007 J. Chem. Phys. 126 064307
[17] Brungery M J and Buckman S J 2002 Phys. Repts. 357 215
[18] Kawahara H, Kato H, Hoshino M, Tanaka H and Brungery M J, 2007 Proc. of 25th. ICPEAC (Freiburg, Germany)
[19] Thorn P A, Brungery M J, Teubner P J O, Diakomichalis N, Maddern T, Boloriazadeh M A, Newell W R, Kato H, Hoshino M, Tanaka H, Cho H, and Kim Y-K 2007 J. Chem. Phys. 126 064306
[20] Lassettre E N and Skerbele A 1974 J. Chem. Phys. 60 2464
[21] Klump K N and Lassettre E N, 1975 Can. J. Phys. 53 1825