Bachelor Thesis Chemistry

Improvement of the zero-point oscillation energy in the strong interaction limit in Density Functional Theory

The Point-Charge-Plus-Continuum Model

by

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1 Abstract

Using Density-Functional Theory, where the electronic density distribution of a system is used, the exact energy of a quantum system can be calculated.[1] However, for many-electron systems, approximations must be made, due to the fact that the calculations become too challenging. This is because the calculations are too demanding as a result of the exchange-correlation energy, which describes the interaction energy between the electrons. In this paper the point-charge-plus-continuum (PC) model, which attempts to approximate the exchange-correlation energy in the strong interaction limit where electrons are infinitely strongly repelling each other will be discussed.[2] The idea behind the PC model is that, instead of a positively attractive nucleus, a uniform positive background is present. Part of the PC model addresses the coefficient \( W'_\infty[\rho] \), which describes the zero-point oscillations that electrons make around their positions. In this paper, it is attempted to improve the PC model \( W'^{PC}_\infty[\rho] \) for \( W'_\infty[\rho] \) by adding a third term to it, including the gradient of the density to the power four. Four modified PC models are presented, which differ by the coefficients of the second and third terms. The errors of these models are calculated by looking at the He isoelectric series and the Hooke series and comparing the obtained values with the exact values of \( W'_\infty[\rho] \). The Hooke atom is an artificial two-electron system, where the electron-nucleus attraction is replaced by a harmonic oscillator potential.[3] Since the Hooke atom and the He isoelectric series are small systems with two electrons, the exact value of \( W'_\infty[\rho] \) can be calculated. By comparing the exact value of \( W'_\infty[\rho] \) and the value obtained using the different PC models, the errors and relative errors of the modified PC models are depicted against the errors of the original PC model. The PC model performs well for the He isoelectric series, where all the errors are smaller than 4% and performs poorly for the Hooke series, where the errors are between 20-100%. 
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2 Introduction

2.1 DFT

In 1926, E. Schrödinger developed the ‘Schrödinger equation’, which in principle could describe the exact quantum state of a system.[4] The Schrödinger equation is an equation for the many-electron wave function $\psi$:

$$\hat{H}\psi = E\psi \quad (1)$$

Here, $E$ is the energy of the system and $\hat{H}$ is the Hamiltonian, which can be split into three parts:[1]

$$\hat{H}\psi = \left[ \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}} \right] \psi = -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - \sum_{j,l} Z_l e^2 |r_j - R_l| + \frac{1}{2} \sum_{j \neq j'} e^2 |r_j - r_{j'}|^2 \psi \quad (2)$$

Here, $\hat{T}$ is the operator of the kinetic energy, $\hat{V}_{\text{ee}}$ is the operator of the potential energy on the electrons, caused by the positively charged nucleus, $\hat{V}_{\text{ext}}$ is the operator of the energy that arises, due to the electron-electron interaction, $\vec{r}_j$ and $\vec{R}_l$ are the positions of the electrons and nuclei respectively and $Z_l$ are the atomic numbers. In principle, this equation can be solved exactly. In practice, however, a problem arises when a many-electron system is calculated. Due to the last part of the Hamiltonian $\hat{V}_{\text{ext}}$, where the interaction energy between the electrons is calculated, an exponential wall arises. The calculations become too demanding due to the fact that all electron-electron interactions should be considered. A different approach to the calculation of the energy of a system is Density-Functional Theory (DFT).

In DFT, not the wave function, but the density distribution $\rho(r)$ plays the central role.[1] The density function is defined as:

$$\rho(r) = N \sum_{s_N} \int d\vec{r}_2... \int d\vec{r}_N |\psi(\vec{r}_1, s_1, \vec{r}_2, s_2... \vec{r}_N, s_N)|^2 \quad (3)$$

where $\psi$ is the N-particle wave function, derived from the Schrödinger equation, $\vec{r}$ and $s$ denote the spatial and spin coefficients respectively and $N$ is a normalization factor. Using this function for the density, a new functional for the energy can be derived:

$$F[\rho] = T_s[\rho] + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\rho(\vec{r}) \rho(\vec{r}' )}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho] \quad (4)$$

where $T_s[\rho(r)]$ is the operator of the kinetic energy functional of the non-interacting electrons. In principle this function can be derived exactly. However, for many-particle systems, a problem arises with the calculation of $E_{xc}[\rho]$, the exchange-correlation energy consisting of two parts, the exchange energy $E_x[\rho]$ and the correlation energy $E_c[\rho]$, which describes the interaction energy between electrons. As with the calculation of $V_{ee}$, where the calculations became
too demanding, this too happens with the calculation of $E_{xc}[\rho]$. For this reason, approximations of the exchange-correlation energy must be made.

A possible way of calculating the functional of the exchange-correlation energy exactly is by using the coupling-constant integral:[5],[6]

$$E^3_{xc}[\rho] = \int_0^\beta d\alpha W_\alpha[\rho]$$

(5)

where $W_\alpha[\rho]$ is defined as:

$$W_\alpha[\rho] = \langle \Psi_\alpha[\rho]|\hat{V}_{ee}|\Psi_\alpha[\rho]\rangle - U[\rho].$$

(6)

Here, $\Psi_\alpha[\rho]$ is a particular N-electron wave function that yields a given density $\rho$ and, at the same time, minimizes the expectation value of $\langle \hat{T} + \alpha \hat{V}_{ee} \rangle$.[7] Because the electron-electron interaction is defined by $\alpha \hat{V}_{ee}$ and not by $\hat{V}_{ee}$, $\langle \Psi_\alpha[\rho]|V_{ee}|\Psi_\alpha[\rho]\rangle$ is not really the interaction energy, but, more precisely, depicts the averaged inverse distance $\frac{1}{|\vec{r} - \vec{r}'|}$ between $\vec{r}$ and $\vec{r}'$. $\alpha$ denotes the repulsion strength between the electrons, for this reason the distance between $\vec{r}$ and $\vec{r}'$ increases when $\alpha$ increases. So $W_\alpha[\rho]$ is a decreasing function of $\alpha$. Because the electrons form a finite density distribution, their distances cannot grow infinitely. Therefore $W_\alpha[\rho]$ has a lower bound $W_\infty[\rho] > -U[\rho]$.

For large systems, finding an exact value for $W_1[\rho]$, where the interaction energy between the electrons is given by $\hat{V}_{ee}$, is not possible because the calculations would be too demanding. Because of this, it has been attempted to interpolate between the two limits of $\alpha \to 0$ and $\alpha \to \infty$. This paper will focus on the limit $\alpha \to \infty$, where the repulsion between electrons is infinitely strong. $W_\alpha[\rho]$ follows the following asymptotic behavior:

$$W_\alpha[\rho] \to W_\infty[\rho] + \frac{W'_\infty[\rho]}{\sqrt{\alpha}} \quad (\alpha \to \infty).$$

(7)

2.2 PC Model

To calculate $W_\alpha[\rho]$ in the strong interaction limit $\alpha \to \infty$, an approximation of $W_\infty[\rho]$ and $W'_\infty[\rho]$ is desirable. A model that has been proposed by M. Seidl et al. is the point-charge-plus-continuum (PC) model.[2] This model is based on the concept of strictly correlated electrons, which describes systems where the electrons are distributed over the density evenly, leading to a smooth density distribution. When $\alpha$ approaches infinity, the repulsion between the electrons becomes infinite and therefore, the external potential, caused by the nucleus, must be replaced by one that becomes as attractive as $\alpha$. Otherwise, the system would not have a smooth density distribution. Now consider a system of two electrons and a nucleus. When the repulsion between the two electrons becomes strong, assuming that one electron would approach the nucleus, the other electron would be pushed away. And when the repulsion becomes infinitely strong, the electrons will be exactly opposite to each other. Because the position
of one electron at \( \vec{r}_1 \) is now dependent on the position of the other electron at \( \vec{r}_2 \). \( \vec{r}_2 \) is an exact function of \( \vec{r}_1 \). These functions are called *co-motion functions*.\[7\] The electrons also perform zero-point oscillations at their strictly correlated positions.\[8\] These oscillations are captured in the term \( W'_\infty[\rho] \). Since \( W_\infty[\rho] \) and \( W'_\infty[\rho] \) cannot be calculated exactly for large systems, an approximation must be made. In the case of this paper, where 2-electron systems are considered, the exact values can be calculated.

When a system of \( N \) electrons is considered, with a small value \( \alpha < 1 \), the electrons are distributed irregularly within the density \( \rho(\vec{r}) \). This changes in the strong interaction limit \( \alpha \to \infty \), as the electrons are strictly correlated, they are distributed smoothly over the density. In the PC model, instead of a positively charged nucleus, a continuous positive background density \( \rho_+(\vec{r}) \) is considered.\[9\] The overall electrostatic energy functional then becomes:

\[
E_{es}[\Psi, \rho_+] = \langle \Psi | \hat{V}_{ee} | \Psi \rangle + U[\rho_+] - e^2 \int d^3r \rho(r) \int d^3r' \frac{\rho_+(\vec{r}')}{|\vec{r} - \vec{r}'|}. \tag{8}
\]

The first term describes the interaction between electrons, the second term the energy of the positive background and the last term the interaction between the electrons and the positive background. When the wave function \( \Psi_\alpha(\vec{r}) \) of Eq. (8) is considered, the expression for \( W_\alpha[\rho] \) turns into:

\[
W_\alpha[\rho] = \langle \Psi_\alpha[\rho] | \hat{V}_{ee} | \Psi_\alpha[\rho] \rangle - U[\rho] = E_{es}[\Psi_\alpha[\rho], \rho]. \tag{9}
\]

Because the electrons are distributed evenly over the density and the background is continuously positive, each electron can be put into a ‘cell’ with a positive background of charge 1. Because one electron is in each cell, the cells are neutral. An example of this is given in Figure 1(a).

![Figure 1: (a) Division of the positive background into polyhedral cells, all with positive charge 1, including one electron, which causes the cells to be neutral. (b) The PC cells, a sphere around an electron, again with a neutral charge.](image)

Since the cells are all neutral, the interaction between them is small, so in the strong-interaction limit \( \alpha \to \infty \), the total electrostatic energy becomes a
sum of the energies of the local contributions of each cell $E_{cell}(C_n)$, with N cells.

$$W_\infty[\rho] = \lim_{\alpha \to \infty} E_{es}[\Psi_\alpha[\rho], \rho] \approx \sum_{n=1}^{N} E_{cell}(C_n)$$

(10)

However, these polyhedral shaped cells are not very useful. Every cell would have a different shape, so finding the optimal shape for the cells is troublesome. This is why the PC cell was introduced, [2] where the cell is a sphere around an electron, still with a positive background of charge 1, which is displayed in Figure 1(b).

In a general case, where a density $\rho$ has a gradient $\nabla \rho$ that is not equal to zero, the gradient is considered to be constant throughout the cell. For this reason, the charge of the cell is still neutral. However, the dipole moment becomes non-zero due to the gradient. This can be accounted for by shifting the cell in the opposite direction of the gradient for a distance $d(\vec{r})$, as shown in Figure 2. As the cell now changes position, the radius of the cell has to be increased to a new radius $R(\vec{r})$ to ensure that the charge of the cell remains zero. Using these two quantities, $d(\vec{r})$ and $R(\vec{r})$, with further calculations one can derive an expression for $W_\infty[\rho]$:

$$W_{\infty}^{PC}[\rho] = e^2 \int d^3\vec{r} \left[ A \rho(\vec{r})^{4/3} + B \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})^{1/3}} \right]$$

(11)

where the constants $A$ and $B$ can be calculated as: $A = -\frac{9}{400\pi} \left( \frac{4\pi}{3} \right)^{1/3} = 1.451$ and $B = \frac{3}{350} \left( \frac{4\pi}{3} \right)^{1/3} = 5.317 \times 10^{-3}$.

![Figure 2](image)

**Figure 2:** To account for the non-zero dipole moment, the cell is shifted in the opposite direction of the gradient by a distance $d(\vec{r})$, causing the cell to increase it’s radius from $r_s$ to $R$.

Testing this PC model led to the conclusion that in the limit of $\alpha \to \infty$ $W_\alpha[\rho]$ becomes a local functional of the density.[7] When a large finite $\alpha \gg$
1 is considered, where electrons perform zero-point oscillations around their equilibrium, this property should still persist. For this reason, \( W'_\infty[\rho] \) should also have a second-order gradient expansion. Using the scaling law \( W'_\infty[\rho] = \lambda^{3/2}W'_\infty[\rho] \), an expression for \( W'_\infty[\rho] \) is found:

\[
W'_\infty[\rho] = e^2a_1/2 \int d^3\vec{r}[C\rho(\vec{r})^{3/2} + D|\nabla\rho(\vec{r})|^2\rho(\vec{r})^{7/6}] \quad (12)
\]

The value of \( C \) was derived to be \( C = \frac{1}{2}(3\pi)^{1/2} = 1.535, [9] \) The value for the gradient coefficient \( D \), however, was derived to be \( D = \frac{1}{40}(\frac{3}{4}\pi)^{1/6} = 0.0197: \) a positive number, where a negative gradient is expected. For this reason a different value for \( D \) should be found, to improve the accuracy of the PC model.

2.3 Calculated Systems

To improve the PC model, the value of \( D = -0.02558 \) was chosen, which is chosen in such a manner that the value of \( W'_\infty^{PC}[\rho] \) and \( W'_\infty^{MGGA}[\rho] \) are identical for the two-electron density of the He atom. [10] The goal of this paper is to determine a better value for \( D \). This is attempted by looking at the He isoelectric series and the series of the Hooke’s atom. Since these are small systems, consisting of only two electrons, the value of \( W'_\infty[\rho] \) can be calculated exactly. By looking at the errors and the relative errors between \( W'_\infty^{PC}[\rho] \) and \( W'_\infty^{exact}[\rho] \) it is attempted to discover a better formula for \( W'_\infty[\rho] \).

2.3.1 He isoelectric series

The first series that is considered is the He isoelectric series. This is a series of ions with different atomic numbers, but all with two electrons. The ions with atomic numbers from 1-10, as well as the artificial ions with atomic numbers of 0.92, 0.93, 0.94 and 0.95 are considered. The two-electron Hamiltonian becomes:

\[
\hat{H}\psi = \left[-\frac{1}{2}\nabla^2_{r_1} - \frac{1}{2}\nabla^2_{r_2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|r_1 - r_2|}\right]\psi. \quad (13)
\]

Because the strong-interaction limit \( Z \to \infty \) is also considered, a change of coordinates, \( s = rZ \), must be made. After this change, the Hamiltonian becomes:

\[
\hat{H}\psi = Z^2\left[-\frac{1}{2}\nabla^2_{s_1} - \frac{1}{2}\nabla^2_{s_2} - \frac{1}{s_1} - \frac{1}{s_2} + \frac{1}{Z}\frac{1}{|s_1 - s_2|}\right]\psi. \quad (14)
\]

Because \( Z \) approaches infinity, the last term, \( \frac{1}{Z}\frac{1}{|s_1 - s_2|} \), becomes zero, so this hamiltonian then describes a non-interacting system.
2.3.2 Hooke

The other system that is considered is the series of the Hooke’s atom, which is an artificial atom which describes a system with two electrons. It differs from a normal system because the Coulomb electron-nucleus attraction is replaced by a harmonic oscillator potential.[3] The energy of this system can be calculated exactly. The Hamiltonian of the Hooke’s atom is:

\[ \hat{H}\psi = \left[ -\frac{1}{2}\nabla^2_1 + \frac{1}{2}\omega^2 r_1^2 - \frac{1}{2}\nabla^2_2 + \frac{1}{2}\omega^2 r_2^2 + \frac{1}{|r_1 - r_2|} \right] \psi. \]  

(15)

When, instead of using \( \vec{r}_1 \) and \( \vec{r}_2 \), the difference vector \( \vec{r} = \vec{r}_2 - \vec{r}_1 \) and the center of mass \( R = \frac{1}{2}(\vec{r}_1 + \vec{r}_2) \) are introduced, the Hamiltonian decouples into:

\[ \hat{H}_r\psi = \left[ -\nabla^2_r + \frac{1}{4}\omega^2 r^2 + \frac{1}{r} - \frac{1}{4}\nabla^2_R + \omega^2 R^2 = \hat{H}_r + \hat{H}_R \right] \psi. \]  

(16)

In Ref. [3], the ground state densities \( \rho \) are given for different values of the frequency \( \omega \). These frequencies are dependent on the number of polynomials in Eq. (17) of Ref. [3]. In Table 1, the corresponding \( \omega \)’s are given for different value’s of \( n \), where \( n \) denotes the amount of terms that are added from the polynomial. In this paper we will focus on the cases where \( n = 1, 2, 4, 6, 8, 9, 10 \), as well as the case where \( \omega \to \infty \).

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>0.0173462</td>
</tr>
<tr>
<td>6</td>
<td>0.0058417</td>
</tr>
<tr>
<td>8</td>
<td>0.0026381</td>
</tr>
<tr>
<td>9</td>
<td>0.0018966</td>
</tr>
<tr>
<td>10</td>
<td>0.001409</td>
</tr>
</tbody>
</table>

As can be seen in Table 1, when \( n \) is increased \( \omega \) becomes smaller, so the density distribution becomes more local. When the density is decreased, the interaction energy contributes more to the properties of the system and the kinetic energy contributes less. For this reason, the Hooke system where \( \omega \to \infty \) is similar to the He isoelectric system where \( Z \to \infty \).
3 Experimental

First, the errors and relative errors between the original PC model $W'_\infty[\rho]$ and the exact functional $W'^{exact}_\infty[\rho]$ are calculated for the He isoelectric series and for the Hooke’s atom. Of the He isoelectric series, the densities of the atoms with atomic number ($Z$) from 1 to 10, as well as the artificial atoms with atomic numbers of 0.92, 0.93, 0.94 and 0.95 and the limit where $Z \to \infty$ are considered. Of the Hooke’s atom, the systems shown in Table 1 and the limit where $\omega \to \infty$ are considered. The manner in which $W'^{exact}_\infty[\rho]$ is calculated can be found in Appendix 7.1.

After calculating the errors, it is attempted to add an extra term to $W'_\infty[\rho]$, including the gradient of the density to the power 4. Using the scaling law $W'_\infty[\rho] = \lambda^{3/2}W'_{\infty}[\rho]$ [7] leads to the following formula:

$$W'^{PCmod}_\infty[\rho] = \int d^3\vec{r}C \rho(\vec{r})^{3/2} + D \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})^{7/6}} + E \frac{|\nabla \rho(\vec{r})|^4}{\rho(\vec{r})^{23/6}}.$$  (17)

This model will be referred to as the modified PC model: $W'^{PCmod}_\infty[\rho]$. The calculation of the new constant $E$ is conducted in two fashions: by keeping the original value of constant $D$, which gives an exact value for the He atom, and by calculating a new value for $D$.

First, the squared difference between $W'^{exact}_\infty[\rho]$ and $W'^{PCmod}_\infty[\rho]$ is calculated for all atoms with atomic numbers from 1 to 10 and the system where $Z \to \infty$ in the He isoelectric series. By minimizing the sum of these squared differences, a new value for $E$ is calculated. The case where a new value for $D$ is also calculated is worked out more explicitly in the Appendix.

Because the values for $W'_\infty[\rho]$ are higher for atoms with a higher atomic number, their contribution to the difference between $W'^{exact}_\infty[\rho]$ and $W'^{PCmod}_\infty[\rho]$ are likewise significantly higher. Therefore, the newly-established errors will be smaller for atoms with a higher atomic number, but greater for atoms with a lower atomic number. To account for this, the value for $E$ has also been calculated after using the appropriate scaling law, $W'_\infty[\rho] = \lambda^{3/2}W'_{\infty}[\rho]$, [7], thus dividing the difference between $W'^{exact}_\infty[\rho]$ and $W'^{PCmod}_\infty[\rho]$ by $Z^{3/2}$. This value will be referred to as scaled $E$.

In this manner, four different modified PC models for $W'_\infty[\rho]$ are introduced: with a new value for $E$, a scaled value for $E$, a new value for $D$ and $E$ and a scaled value for $D$ and $E$. The errors and relative errors between $W'^{exact}_\infty[\rho]$ and $W'^{PCmod}_\infty[\rho]$ are calculated for these four modified PC models for the He isoelectric series and for the Hooke’s atom and compared with the errors of the original model.
4 Results

In Table 2, the values for D and E of the four different modified PC models are presented.

<table>
<thead>
<tr>
<th></th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original D and new value for E</td>
<td>-0.02558</td>
<td>-3.66435 \cdot 10^{-7}</td>
</tr>
<tr>
<td>Original D and new value for E (scaled)</td>
<td>-0.02558</td>
<td>-3.24662 \cdot 10^{-7}</td>
</tr>
<tr>
<td>New value for D and E</td>
<td>-0.02918</td>
<td>3.05738 \cdot 10^{-7}</td>
</tr>
<tr>
<td>New value for D and E (scaled)</td>
<td>-0.02882</td>
<td>-7.01521 \cdot 10^{-7}</td>
</tr>
</tbody>
</table>

4.1 Original D and new value for E

In this section, the errors \((W'_{\infty}^{\text{exact}}[\rho] - W'_{\infty}^{\text{PCmod}}[\rho])\) and relative errors \(((W'_{\infty}^{\text{exact}}[\rho] - W'_{\infty}^{\text{PCmod}}[\rho]) / W'_{\infty}^{\text{exact}}[\rho])\) for the modified PC model, where the original value of D is fixed when calculating the value for E, are shown in three different figures. All errors are depicted against \(1/Z\) and for the Hooke series against \(1/\omega\), due to the fact that the limits \(Z \rightarrow \infty\) and \(\omega \rightarrow \infty\) are also considered. To account for the fact that the energy calculated in the \(Z \rightarrow \infty\) limit is divided by \(Z^{3/2}\), due to the scaling law \(W'_{\infty}[\rho_{\lambda}] = \lambda^{3/2} W'_{\infty}[\rho][7]\), all errors given in Figure 3 are likewise divided by \(Z^{3/2}\). For the Hooke’s atom, the scaling factor \(\lambda\) is \(\sqrt{\omega}\), using this factor and the same scaling law, all errors in the Hooke series are divided by \(\omega^{3/4}\).

Figure 3: The errors of \(|W'_{\infty}^{\text{exact}}[\rho] - W'_{\infty}^{\text{PCmod}}[\rho]| / Z^{3/2}\) of the He isoelectric series against \(1/Z\). The blue line shows the errors of the original PC model and the orange and green line show the errors of the modified PC model with the original value of D and the scaled model respectively. The right-hand figure shows the same errors for all calculated systems with \(Z \geq 2\).
Figure 4: The relative errors of $W_{\infty}^{exact}[\rho] - W_{\infty}^{PC mod}[\rho]$ of the He isoelectric series against $1/Z$. The blue line shows the relative errors of the original PC model and the orange and green line show the relative errors of the modified PC model with the original value of $D$ and the scaled model respectively. The right-hand figure shows the same errors for all calculated systems with $Z \geq 2$.

Figure 5: The errors of $|W_{\infty}^{exact}[\rho] - W_{\infty}^{PC mod}[\rho]|/\omega^{3/4}$ of the Hooke series against $1/\omega$. The blue line shows the errors of the original PC model and the orange and green line show the errors of the modified PC model with the original value of $D$ and the scaled model respectively. The right-hand figure shows the relative errors.
4.2 New value for D and E

In this section, the results for the errors and relative errors are given for the modified PC model with a new value for D and E. This is done in the same manner as in section 4.1.

Figure 6: The errors of $|W_{\infty}^{\text{exact}}[\rho] - W_{\infty}^{\text{PC mod}}[\rho]|/Z^{3/2}$ of the He isoelectric series against $1/Z$. The blue line shows the errors of the original PC model and the orange and green line show the errors of the modified PC model with the new values for D and E and the scaled model, respectively. The right-hand figure shows the same errors for all calculated systems with $Z \geq 2$.

Figure 7: The relative errors of $|W_{\infty}^{\text{exact}}[\rho] - W_{\infty}^{\text{PC mod}}[\rho]|$ of the He isoelectric series against $1/Z$. The blue line shows the relative errors of the original PC model and the orange and green line show the relative errors of the modified PC model with the new values for D and E and the scaled model respectively. The right-hand figure shows the same errors for all calculated systems with $Z \geq 2$. 
Figure 8: The errors of $|W_\infty^{\text{exact}}[\rho] - W_\infty^{\text{PCmod}}[\rho]|/\omega^{3/4}$ of the Hooke series against $1/\omega$. The blue line shows the errors of the original PC model and the orange and green line show the errors of the modified PC model with the new values for $D$ and $E$ and the scaled model respectively. The right-hand figure shows the relative errors.
5 Discussion

In this sections, the results presented in Figures 3-8 and Table 2 will be discussed to verify if the modified PC models give an improvement on the original model. This is split into two parts: where the original value for D is kept and where a new value for D is considered.

5.1 Original D and new value for E

When the blue lines in Figure 3 and 4 are examined, the error of the PC model for the He atom is naturally zero, because in the original PC model the parameter D was adjusted to the He atom. When Z is increased, the error of $W'_\infty[\rho]$ also increases, except for the case where $Z \to \infty$, where the error is smaller than for the cases with high Z. All errors for the ions with $Z \geq 2$, are under 1%. For the ions with $Z \leq 2$, the errors are larger, ranging from 2-4%. The reason that the blue line, which represents the errors of the original PC model in Figures 3-8, is not smooth, is because the used densities were not accurate enough.

The errors of the Hooke series increase with decreasing $\omega$, as can be seen by the blue line in Figure 5. The errors are significantly higher than the errors of the He series, ranging from a 20% error for the systems with large $\omega$, where $n$ is small, and 80% for the system with small $\omega$, where $n$ is large. Because the density becomes more local for systems with small $\omega$, the gradient of the system will increase, causing the PC model to be less accurate.

When the modified PC model with the original D and the newly-calculated value for E is considered (Figure 3 and 4), it can be seen that the scaled (green line) and unscaled (orange line) models produce similar results for the He iso-electric series. The errors are smaller than the errors of the original model for systems where $Z > 2$. However, the errors are larger for systems where $Z \leq 2$. Figure 5 shows that the modified PC model produces less accurate results for the Hooke series. The scaled and unscaled model show the same pattern as the original model and produce similar results, with the scaled model producing slightly better results.

Because the scaled and unscaled models perform similarly in both series, it can be concluded that the scaling did not effect this model very much. This is confirmed by the fact that the difference between the two calculated values for E, which are shown in Table 1, is small. An approach to improve the scaled model and consequently obtain better results in the He series for systems where $Z < 2$, a different scaling factor could be used, where the errors of the systems where $Z < 2$ weigh heavier, when calculating the scaled value of E.

5.2 New value for D and E

After considering the PC model where the original value for D is kept, the case where a new value for D and E is calculated, is now considered. When Figure’s 6 and 7 are examined, where the errors and relative errors of the scaled and unscaled modified PC model with a new value for D and E are depicted against
the original errors of the He series, a different pattern is found. Firstly, the scaled and unscaled models give a different pattern, whereas the scaled and unscaled model with the original value for D give similar results. Again, the errors for the systems where \( Z \geq 2 \) are smaller than the errors of the original system, with the exception of the scaled model, which now gives a less accurate result for the Li\(^+\) ion. The errors found of the unscaled model for the systems where \( Z < 2 \) give less accurate results than the original model. However, for the scaled model the errors are smaller than the original model. Thus the scaled modified PC model provides a slight improvement to the original model for all calculated systems in the He series, except for He and Li\(^+\).

When Figure 8 is considered, it can be seen that the scaled model gives less accurate results for the Hooke series than the original model. It also has a different pattern, having a decreasing error when \( \omega \) decreases. This difference in pattern can be explained by looking at the calculated values for E in Table 1. For the unscaled model, the value for E is positive and for the scaled model the value for E is negative. When \( \omega \) is increased, the density distribution becomes more local, because of this the gradient increases. Since the factor E precedes a term which includes the gradient to the power 4, when E is positive, the error will be an increasing function when \( \omega \) becomes smaller. However, when E is negative, the contribution of the gradient could cause the function to decrease when \( \omega \) becomes small, which is the case with the modified scaled PC model. The unscaled system is the only modified model that gives slightly better results for the Hooke series than the original.

The modified PC models have been used to calculate the \( W'_\infty[\rho] \) of two-electron systems. The modified model with a scaled value for D and E gives a slight improvement on the He isoelectric series and the unscaled model gives a slight improvement on the Hooke series. To verify whether the modified PC models might be an improvement on the original PC model, an idea would be to use the modified PC models on other systems, such as small molecules, and check how they perform then. After examining other systems, it might be verified to see whether the modified PC model is an improvement and whether it might be adopted for further use.
6 Conclusion

In conclusion, the errors and relative errors for four different modified PC models have been depicted against the original errors of the PC model. These errors were calculated for the He isoelectric series and for the Hooke series. The PC model performs significantly better for the He isoelectric series, having relative errors under 5%, where the relative errors for the Hooke series range from 20-100%.

The exchange-correlation energy can be calculated using the coupling-constant integral.[5][6] Because this cannot be calculated exactly, it is attempted to interpolate between the two interaction limits $\alpha \to 0$ and $\alpha \to \infty$, the limits with no interaction and infinitely strong interaction. To calculate the infinitely strong interaction limit, i.e. strictly correlated systems, $W_{\alpha}^\prime[\rho]$ needs to be calculated. To calculate $W_{\alpha}^\prime[\rho]$, the PC model was introduced.[2] This model describes a system where the electrons are distributed over a positively charged background. To improve this model, four different modified PC models are introduced. The errors of these models were calculated using the exact value’s of $W_{\alpha}^\prime[\rho]$ and depicted against the original PC model. The scaled model with a new calculated value for D and E gives smaller errors for the He isoelectric series, excluding He and Li$^+$ and the unscaled model gives smaller errors for the Hooke system. However, the improvements were not significant enough to verify that the modified models are an improvement on the original model. To evaluate whether the modified PC models could be utilized in the future, other systems, such as small molecules, should be considered using the modified PC models.
7 Appendix

7.1 Calculation of $W^\text{exact}_{\infty}[\rho]$

From a given density $\rho(\vec{r})$, $N_e(\vec{r})$ can be calculated:

$$N_e(\vec{r}) = \int_0^\infty dx 4\pi x^2 \rho(x)$$  \hspace{1cm} (18)

Since only two-electron systems are considered, there is only one co-motion function, which can be calculated from $N_e[\vec{r}]$ and it’s inverse $N_e^{-1}[\vec{r}]$:

$$f(\vec{r}) = N_e^{-1}(2 - N_e(\vec{r}))$$ \hspace{1cm} (19)

From the co-motion function the next three equations are obtained:

$$f_1(\vec{r}) = \frac{-\rho(\vec{r})\vec{r}^2}{\rho(f(\vec{r}))f(\vec{r})^2}$$ \hspace{1cm} (20)

$$k_1(\vec{r}) = \frac{\vec{r}^2 + f(\vec{r})^2}{f(\vec{r})(\vec{r}^2 + f(\vec{r}))^3}$$ \hspace{1cm} (21)

$$k_2(\vec{r}) = \frac{2(1 + f_1(\vec{r})^2)}{(\vec{r}^2 + f(\vec{r}))^3 f_1(\vec{r})}$$ \hspace{1cm} (22)

From these functions, the exact value of $W^\text{exact}_{\infty}[\rho]$ can be calculated:

$$W^\text{exact}_{\infty}[\rho] = \int_0^{N_e^{-1}[1]} dx 4\pi x^2 (2\sqrt{k_1(x)} + \sqrt{k_2(x)}) \rho(x)$$ \hspace{1cm} (23)

7.2 Calculating a new value for D and E

In the modified PC model the following functionals are defined:

$$I_0[\rho] = \int d^3\vec{r} \rho(\vec{r})^{3/2}$$ \hspace{1cm} (24)

$$I_2[\rho] = \int d^3\vec{r} |\nabla \rho(\vec{r})|^2 \rho(\vec{r})^{7/6}$$ \hspace{1cm} (25)

$$I_4[\rho] = \int d^3\vec{r} |\nabla \rho(\vec{r})|^4 \rho(\vec{r})^{23/6}$$ \hspace{1cm} (26)

In terms of these functionals, the sum of the squared difference between $W^\text{exact}_{\infty}[\rho]$ and $W^\text{PCmod}_{\infty}[\rho]$ are defined as:

$$f(D, E) = \sum_{Z=1}^{10} (CI_0[\rho] + DI_2[\rho] + EI_4[\rho] - W^\text{exact}_{\infty}[\rho])^2$$ \hspace{1cm} (27)
This can be simplified into:

\[ f(D, E) = a_{11}D^2 + a_{12}DE + a_{22}E^2 + b_1D + b_2E + c \]  \hspace{1cm} (28)

with the following coefficients:

\[ a_{11} = \sum_{Z=1}^{10} I_2[\rho_Z]^2, \]  \hspace{1cm} (29)

\[ a_{12} = 2 \sum_{Z=1}^{10} I_2[\rho_Z]I_4[\rho_Z], \]  \hspace{1cm} (30)

\[ a_{22} = \sum_{Z=1}^{10} I_4[\rho_Z]^2, \]  \hspace{1cm} (31)

\[ b_1 = 2 \sum_{Z=1}^{10} (C I_0[\rho_Z] - W_{\infty}^{\text{exact}}[\rho_Z])I_2[\rho_Z], \]  \hspace{1cm} (32)

\[ b_2 = 2 \sum_{Z=1}^{10} (C I_0[\rho_Z] - W_{\infty}^{\text{exact}}[\rho_Z])I_4[\rho_Z], \]  \hspace{1cm} (33)

\[ c = \sum_{Z=1}^{10} (C I_0[\rho_Z] - W_{\infty}^{\text{exact}}[\rho_Z])^2. \]  \hspace{1cm} (34)

where \( \rho_Z(r) \) defines the density of the He isoelectric ion with nuclear charge \( Z \).

To minimize this function, the conditions \( \frac{\partial f(D,E)}{\partial D} = \frac{\partial f(D,E)}{\partial E} = 0 \) are used. This leads to the following two equations, which can be solved exactly:

\[ 2a_{11}D + a_{12}E + b_1 = 0 \]  \hspace{1cm} (35)

\[ 2a_{22}E + a_{12}D + b_2 = 0 \]  \hspace{1cm} (36)

Solving these equations leads to a value of \( D \) and \( E \), which minimize the sum of the squared difference between \( W_{\infty}^{\text{exact}}[\rho] \) and \( W_{\infty}^{\text{PCmod}}[\rho] \).

To find the value of the \textit{scaled} \( D \) and \( E \), \( I_0[\rho] \), \( I_2[\rho] \) and \( I_4[\rho] \) are divided by \( Z^{3/2} \), as follows from the scaling law \( W^\nu_\infty[\rho_\lambda] = \lambda^{3/2}W^\nu_\infty[\rho] \). After that, the same calculations are performed.
References


