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The question of the completeness of the natural orbitals with nonzero occupation numbers for atoms and molecules

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Summary. The completeness of the natural orbitals with nonzero occupation numbers is examined for several model Hamiltonians and for the helium atom. It is demonstrated that whether the occupied natural orbitals form complete sets depends on the nature of the electron-electron interaction in the model Hamiltonian. Discrepancies in the extant proofs of the exactness and inexactness of the extended Koopmans' theorem are resolved.

Key words: Reduced density matrices – Natural orbitals – Extended Koopmans' theorem

1 Introduction

One of the fascinating unanswered questions in the study of the reduced density matrices is whether the natural orbitals with nonzero occupation numbers (occupied NO's) for the exact wavefunctions of atoms and molecules form complete sets. An equivalent question is whether a complete basis set is needed to obtain the exact wavefunction in a configuration interaction calculation. It would seem that an appropriate starting point for answering this question would be the helium atom. However, even here, where it is thought that the occupied NO's form a complete set, there seems to be no rigorous proof. An ancillary question is to what extent does the completeness of the occupied NO's depend on the nature of the electron-electron interaction potential. In this paper we discuss several exactly-soluble model systems which can be examined analytically and we examine the question of the completeness of the occupied natural spin orbitals, without proof, for helium.

The first-order reduced density matrix is defined by [1, 2]:

$$\gamma(\vec{x}, \vec{x}') = N \int \Psi(\vec{x}, \vec{x}_2 \ldots \vec{x}_N)\Psi^*(\vec{x}', \vec{x}_2 \ldots \vec{x}_N)\, d\vec{x}_2 \ldots d\vec{x}_N. \quad (1)$$

The variable $\vec{x}_i$ represents the space, $\vec{r}_i$, and spin, ξ_i, coordinates of the ith electron. The density matrix can be written as:

$$\gamma(\vec{x}, \vec{x}') = \gamma_\alpha(\vec{r}, \vec{r}')\alpha(\xi)\alpha(\xi') + \gamma_\beta(\vec{r}, \vec{r}')\beta(\xi)\beta(\xi'). \quad (2)$$

The density matrix can also be written in terms of the natural spin orbitals NO's as:

$$\gamma(\vec{x}, \vec{x}') = \sum_i n_i \chi_i(\vec{x}) \chi_i^*(\vec{x}') \tag{3}$$

where the n_i are the NSO occupation numbers. In what follows we will use $\varrho(\vec{r}, \vec{r}')$ which is given by:

$$\varrho(\vec{r}, \vec{r}') = \gamma_\alpha(\vec{r}, \vec{r}') + \gamma_\beta(\vec{r}, \vec{r}'). \tag{4}$$

The reduced density matrix $\varrho(\vec{r}, \vec{r}')$ can be expanded in terms of the NO's $\chi_i'(\vec{r})$:

$$\varrho(\vec{r}, \vec{r}') = \sum_i n_i' \chi_i(\vec{r}) \chi_i^*(\vec{r}'), \tag{5}$$

where n_i' are the NO occupation numbers. We will use the convention that the NSO or NO is occupied if n_i or $n_i' > 0$, and unoccupied if n_i or $n_i' = 0$. The following two lemmas will be used in our discussions.

Lemma 1. Let $\varrho(\vec{r}, \vec{r}')$ be a first-order reduced density matrix defined by Eq. (4) and $\{f_n\}$ be a complete set. Define:

$$g_n(\vec{r}) \equiv \int \varrho(\vec{r}, \vec{r}') f_n(\vec{r}') \, d\vec{r}'. \tag{6}$$

Then all of the occupied NO's for $\varrho(\vec{r}, \vec{r}')$ form a complete set if and only if $\{g_n\}$ is complete.

Proof. The condition is necessary since if $\{g_n\}$ is not complete we can always find a nonzero function that is orthogonal to the subspace spanned by $\{g_n\}$, say the function $h(\vec{r})$:

$$\int h(\vec{r}) g_n(\vec{r}) \, d\vec{r} = 0, \tag{7}$$

for all n. This can also be written as:

$$\iint h(\vec{r}) \varrho(\vec{r}, \vec{r}') f_n(\vec{r}') \, d\vec{r}' \, d\vec{r} = 0, \tag{8}$$

for all n. Since $\{f_n\}$ is complete we have:

$$\int h(\vec{r}) \varrho(\vec{r}, \vec{r}') \, d\vec{r} = 0. \tag{9}$$

The incompleteness of $\{g_n\}$ means the existence of one or more nonzero NO's of zero occupancy for $\varrho(\vec{r}, \vec{r}')$. We can see that the condition is sufficient from Eqs. (7) and (9). The zero occupation number would mean that the corresponding NO is zero.

Lemma 2. Let $\Psi(\vec{r}_1, \vec{r}_2)$ be a wavefunction for a two particle system, $\varrho(\vec{r}_1, \vec{r}_1')$ be its corresponding first-order reduced density matrix, and $\{f_n\}$ be a complete set. Define:

$$\phi_n(\vec{r}) = \int \Psi(\vec{r}_2, \vec{r}) f_n(\vec{r}_2) \, d\vec{r}_2. \tag{10}$$

Then all of the occupied NO's for $\varrho(\vec{r}_1, \vec{r}_1')$ form a complete set if and only if $\{\phi_n\}$ is complete.

Proof. Define:

$$\begin{aligned} g_n(\vec{r}_1) &\equiv \int \varrho(\vec{r}_1, \vec{r}_1') f_n(\vec{r}_1') \, d\vec{r}_1', \\ &= \iint \Psi^*(\vec{r}_1, \vec{r}_2) \Psi(\vec{r}_1', \vec{r}_2) f_n(\vec{r}_1') \, d\vec{r}_1' \, d\vec{r}_2, \\ &= \int \Psi^*(\vec{r}_1, \vec{r}_2) \phi_n(\vec{r}_2) \, d\vec{r}_2. \end{aligned} \tag{11}$$

Since both $\{\phi_n\}$ and $\{f_n\}$ are complete sets the transformation between the two is nonsingular. Express $\{\phi_n\}$ as:

$$\phi_n(\vec{r}) = \sum_i A_{in} f_{\dot{z}}(\vec{r}), \tag{12}$$

where A is a nonsingular matrix. This gives:

$$g_n = \sum_i A_{in} \phi_i, \tag{13}$$

and $\{g_n\}$ is a complete set. Lemma 2 is proved from Lemma 1.

2 Two cases with no interacting potential

The hydrogen atom having only one electron has no electron-electron interaction potential and the density matrix for any state is just the product of two hydrogenic orbitals. Hence there is only one occupied NO and the set is not complete.

Consider the model two-electron Hamiltonian for helium where the electron repulsion term is zero. Here we have just a single determinant and all of the NSO's have zero occupation number except the two spin orbitals in the determinant. Again the set of occupied NSO's is not complete. The same could of course be said for a model many-electron Hamiltonian where there are no electron repulsion terms.

3 Two coupled one-dimensional harmonic oscillators

The equation for the coupled one-dimensional harmonic oscillator is:

$$-\frac{1}{2}\frac{d^2}{dx_1^2} - \frac{1}{2}\frac{d^2}{dx_2^2} + \frac{1}{2}k(x_1^2 + x_2^2) - \frac{1}{2}\alpha(x_1 - x_2)^2. \tag{14}$$

This equation is separable in the coordinates $X = (x_1 + x_2)/\sqrt{2}$ and $x = (x_1 - x_2)/\sqrt{2}$, and it has the exact solution:

$$\Psi(X, x) = \left(\frac{k^{1/2}}{\pi}\right)^{1/4} \exp\left(-\frac{1}{2}k^{1/2}X^2\right)\left(\frac{K^{1/2}}{\pi}\right)^{1/4} \exp\left(-\frac{1}{2}K^{1/2}x^2\right), \tag{15}$$

which in terms of x_1 and x_2 is:

$$\Psi(x_1, x_2) = \left(\frac{k^{1/2}K^{1/2}}{\pi^2}\right)^{1/4} \exp\left(-\frac{1}{4}(k^{1/2} + K^{1/2})(x_1^2 + x_2^2)\right) \times \exp\left(-\frac{1}{2}(k^{1/2} - K^{1/2})x_1 x_2\right), \tag{16}$$

where $K = (k - 2\alpha)$.

In order to determine whether the NO's of this system all have nonzero occupation numbers we look at the generalized overlap amplitudes [3] of the system. They are defined by:

$$\Phi_n(\vec{x}) = \int \Psi_0(\vec{x}, \vec{x}_2, \ldots, \vec{x}_N)^* \Psi_n^{N-1}(\vec{x}_2, \ldots, \vec{x}_N)\, d\vec{x}_2, \ldots, d\vec{x}_N, \tag{17}$$

where Ψ_0^N is the ground state wavefunction of the N-particle system and $\Psi_n^{(N-1)}$ is the wavefunction for the nth state of the $N - 1)$-particle system. There are also overlap amplitudes associated with the $(N+1)$-particle states:

$$\chi_n(\vec{x}) = \int \Psi_0^N(\vec{x}_2, \ldots, \vec{x}_{N+1})^* \Psi_n^{N+1}(\vec{x}, \vec{x}_2, \ldots, \vec{x}_{N+1})\, d\vec{x}_2, \ldots, d\vec{x}_{N+1} \tag{18}$$

Together the ϕ_n and the χ_n form a complete set [3]. This does not imply that either the set $\{\phi_n\}$ or the set $\{\chi_n\}$ is not complete by itself. The set $\{\phi_n\}$ is the same size as the set of natural orbitals with nonzero occupation numbers, therefore if the set $\{\phi_n\}$ can be shown to be complete, the set of natural orbitals with nonzero occupation numbers is also complete. The generalized overlap amplitudes for the one-dimensional harmonic oscillator are defined by:

$$\phi_n = \int \Psi(x_1, x_2) f_n(x_2)\, dx_2. \tag{19}$$

The $f_n(x_2)$ is the one-particle harmonic oscillator wavefunction for the nth state which is

$$f_n = \frac{1}{(2^n n!)^{1/2}} \left(\frac{k^{1/2}}{\pi}\right)^{1/4} \exp\left(-\frac{k^{1/2}}{2} x^2\right) H_n(k^{1/4}x). \tag{20}$$

$H_n(k^{1/4}x)$ is the Hermite polynomial which can be obtained easily from the following generating function:

$$\exp(-s^2 + 2us) = \sum_{n=0}^{\infty} \frac{s^n}{n!} H_n(u). \tag{21}$$

It is routine to carry out the integration in Eq. (19) by using the generating function for the Hermite polynomial. The result is:

$$\phi_n(x) = C_n H_n(tx) \exp(-\beta x^2/2), \tag{22}$$

with

$$\begin{aligned} C_n &= \sqrt{\frac{(K^{1/2} - k^{1/2})^n}{2^{n-2} n! (3k^{1/2} + K^{1/2})^{n+1}}} \left(\frac{kK^{1/2}}{\pi}\right)^{1/4} \\ t &= k^{1/4} \sqrt{\frac{K^{1/2} - k^{1/2}}{3k^{1/2} + K^{1/2}}} \\ \beta &= \frac{k + 3(kK)^{1/2}}{3k^{1/2} + K^{1/2}}. \end{aligned} \tag{23}$$

There is a one-to-one correspondence between ϕ_n's and the harmonic oscillator wavefunctions. Therefore $\{\phi_n\}$ is a complete set. Lemma 2 implies that the set of NO's with nonzero occupation numbers form a complete set. It should be noted that the $\{\phi_n\}$ is complete by itself without the χ_n.

The elements of the first-order density matrix in the basis of harmonic oscillator eigenfunctions are related to the overlap of the generalized overlap amplitudes:

$$\gamma_{mn} = S_{mn}(\alpha\alpha + \beta\beta), \tag{24}$$

where

$$\begin{aligned} S_{mn} &= \int \phi_m^*(x) \phi_n(x)\, dx \\ &= 4 \left(\frac{m! n! \delta (1-\delta)^{m+n} (-1)^{n-m}}{(3+\delta)^{m+n+1} (1+3\delta)^{m+n+1}}\right)^{1/2} \sum_{p=0}^{[m/2]} \frac{(1+\delta)^{[(n-m)/2]+2p} (1-\delta)^{m-2p}}{p! (m-2p)! \left(\dfrac{n-m}{2} + p\right)!}. \end{aligned} \tag{25}$$

Here $m \leqslant n$ and $\delta = (K/k)^{1/2}$. For $m = n = 0$ this gives:

$$S_{00} = 4\left(\frac{\delta}{(3+\delta)(1+3\delta)}\right)^{1/2}. \tag{26}$$

The case where $\alpha = 0$ gives $\delta = 1$ and $S_{00} = 1$. The element S_{00} goes to zero as $\alpha \to k/2$ and $\delta \to 0$. A measure of the idempotency of the density matrix is given by:

$$Id = Tr(\gamma) - Tr(\gamma^2) = 2 - \frac{4\delta^{1/2}}{1+\delta}. \tag{27}$$

The occupation numbers all tend toward zero as α approaches $k/2$ as can be seen from a plot of $Tr(\gamma) - Tr(\gamma^2)$ in Fig. 1. This is in contrast to a model two-electron ion where the highest NSO occupation numbers approach 1/2 and the others approach zero as the nuclear charge is lowered to the point where the total energy is zero [2].

4 Two coupled isotropic three-dimensional harmonic oscillators

The Hamiltonian for two coupled, isotropic, three-dimensional harmonic oscillators is:

$$-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 + \tfrac{1}{2}k(r_1^2 + r_2^2) - \tfrac{1}{2}\alpha(\vec{r}_1 - \vec{r}_2)^2. \tag{28}$$

The solution is just the product of the solutions to Eq. (14):

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi(x_1, x_2)\Psi(y_1, y_2)\Psi(z_1, z_2). \tag{29}$$

The generalized overlap amplitudes are:

$$\Phi_{n,l,m}(x, y, z) = \phi_n(x)\phi_l(y)\phi_m(z). \tag{30}$$

Again we see that the generalized overlap amplitudes form a complete set and are in one-to-one correspondence with the three-dimensional harmonic oscillator functions. Lemma 2 implies that the NO's with nonzero occupation numbers for the coupled two-particle, three-dimensional harmonic oscillator form a complete set.

5 Two harmonic oscillators coupled by an inverse quadratic repulsion

Another example of an exactly soluble two-electron model is [4]:

$$-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 + \frac{\omega^2}{2}(r_1^2 + r_2^2) + \frac{\lambda}{(\vec{r}_1 - \vec{r}_2)^2}. \tag{31}$$

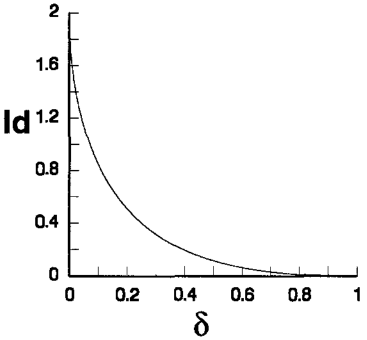

Fig. 1. A plot of $Id = Tr(\gamma) - Tr(\gamma^2)$ versus δ

This has the ground state solution:

$$\Psi(\vec{r}_1, \vec{r}_2) = C \exp[-\omega(r_1^2 + r_2^2)] r_{12}^{\alpha}. \tag{32}$$

where $\alpha = [(1+4\lambda)^{1/2} - 1]/2$. C is a normalization constant. Define:

$$\phi_{mnk}(\vec{r}_1) = \int \Psi(\vec{r}_1, \vec{r}_2) f_{mnk}(\vec{r}_2)\, d\vec{r}_2, \tag{33}$$

with

$$f_{mnk}(\vec{r}) = \exp(-tr^2/2) H_m(t^{1/2}x) H_n(t^{1/2}y) H_k(t^{1/2}z). \tag{34}$$

The set $\{f_{mnk}\}$ is complete in $L^2(R^3)$.

We define:

$$\begin{aligned}\Omega &\equiv \sum_{mnk} \frac{S_x^m S_y^n S_z^k}{m!n!k!} \phi_{mnk}(\vec{r}_1)\\ &= \int \Psi(\vec{r}_1, \vec{r}_2) \exp\left[-\frac{t}{2} r_2^2 - s^2 + 2t^{1/2}\vec{s} \cdot \vec{r}_2\right] d\vec{r}_2.\end{aligned} \tag{35}$$

The second equality in Eq. (35) comes from Eqs. (21), (33), and (34). We obtain Ω in terms of the degenerate hypergeometric function [5]:

$$\begin{aligned}\Omega &= A \exp\left(-\left(2\omega + \frac{t}{2}\right) r_1^2 - s^2 + 2t^{1/2}\vec{s} \cdot \vec{r}_1\right)\\ &\quad\times \Phi\left(\frac{\alpha+3}{2}, \frac{3}{2}; \frac{2\left[t^{1/2}\vec{s} - \left(\omega + \frac{t}{2}\right)\vec{r}_1\right]^2}{2\omega + t}\right),\end{aligned} \tag{36}$$

with

$$A = \frac{(2\pi)^{3/2} C \Gamma(\alpha+2)}{(2\omega+t)^{(\alpha+3)/2} 2^{(\alpha+2)/2} \Gamma\left(\frac{\alpha+2}{2}\right)}, \tag{37}$$

and $\Phi(\beta, \gamma; z)$ is given by:

$$\begin{aligned}\Phi(\beta, \gamma; z) &= 1 + \frac{\beta}{\gamma}\frac{z}{1!} + \frac{\beta(\beta+1)}{\gamma(\gamma+1)}\frac{z^2}{2!} + \frac{\beta(\beta+1)(\beta+2)}{\gamma(\gamma+1)(\gamma+2)}\frac{z^3}{3!} + \cdots\\ &\equiv \sum_{n=0}^{\infty} a_n(\beta, \gamma)\frac{z^n}{n!}.\end{aligned} \tag{38}$$

We choose:

$$t = 2\omega, \tag{39}$$

and obtain Ω:

$$\Omega = A \sum_{l,p,q=0}^{\infty} \phi_{lpq} s_x^l s_y^p s_z^q, \tag{40}$$

with

$$\begin{aligned}\phi_{lpq} &= A \exp(-\omega r_1^2) \sum_{m=0}^{[1/2]} \sum_{i=0}^{[p/2]} \sum_{j=0}^{[q/2]} \frac{(-1)^{m+i+j} l!p!q!a_K\left(-\frac{\alpha}{2}, \frac{3}{2}\right)}{m!i!j!(l-2m)!(p-2i)!(q-2j)!}\\ &\quad\times \Phi\left(K - \frac{\alpha}{2}, K + \frac{3}{2}; -tr_1^2\right)(2t^{1/2}x_1)^{l-2m}(2t^{1/2}y_1)^{p-2i}(2t^{1/2}z_1)^{q-2j}.\end{aligned} \tag{41}$$

Here $K = l + p + q - m - i - j$. When α is any positive even integer the set $\{\phi_{lpq}\}$ is not complete because $a_{\alpha/2+1}(-\alpha/2, 3/2) = 0$ when α is even. Another case of interest which is unphysical [4] is when $\alpha = -3$. Then the set $\{\phi_{lpq}\}$ is complete. Here $\Phi(\beta, \beta; z) = \exp(z)$ and:

$$\phi_{lpq} = A \exp(-(\omega + t)r_1^2)H_l(2t^{1/2}x_1)H_p(2t^{1/2}y_1)H_q(2t^{1/2}z_1). \tag{42}$$

This is a complete set. It is not known whether other values of α would produce occupied NO's that are complete sets, but it seems reasonable to conjecture that there would be physically relevant cases where the occupied NO's would be complete.

As an example of the incompleteness of the occupied NO's for even α we can construct the NO's for $\alpha = 2$.

$$\chi_1(\vec{r}) = \left[\frac{a}{2a + \frac{3}{2}}\left(\frac{2\omega}{\pi}\right)^{3/2}\right]^{1/2}\left[\frac{\omega}{a}r^2 + 1\right]\exp(-\omega r^2),$$

$$\chi_2(\vec{r}) = \left[\frac{a}{2a - \frac{3}{2}}\left(\frac{2\omega}{\pi}\right)^{3/2}\right]^{1/2}\left[\frac{\omega}{a}r^2 - 1\right]\exp(-\omega r^2), \tag{43}$$

$$\chi_{4+m}(\vec{r}) = \left[\frac{3}{32\omega^2}\left(\frac{\pi}{2\omega}\right)^{1/2}\right]^{-1/2} r\exp(-\omega r^2)Y_{lm}(\theta, \phi),$$

where $a = (15)^{1/2}/4$ and $m = -1, 0, 1$. The NO occupation numbers are $n_1 = 4(1 + a)/5$, $n_2 = 4(1 - a)/5$, $n_3 = n_4 = n_5 = 2/15$. [That n_1 is larger than 1 is explained by spin considerations: values of NSO occupation numbers should be half of values of corresponding NO occupation numbers.]

6 The helium atom

The ^1S helium atom wavefunction can be written in terms of its NO's as [2, 6]:

$$\Psi(\vec{x}_1, \vec{x}_2) = \sum C_i\phi_i(\vec{r}_1)\phi_i(\vec{r}_2)\eta(\xi_1\xi_2), \tag{44}$$

where $\eta(\xi_1\xi_2)$ is the appropriate spin function. The NSO occupation numbers of the helium atom are just the squares of the CI coefficients in the NO basis. For singlet states the NO's for both spin types are the same, so the NO's and the spatial part of the natural spin orbitals are the same. A question which arises is whether there are any unoccupied NSO's (NO's) for the exact wavefunction.

Let's assume the above expansion is exact with n terms; it contains all occupied NSO's. To answer the question whether any others will lower the energy we examine the Hamiltonian matrix over configurations constructed from NSO's and add a row and column corresponding to the $(n + 1)$th term. The off-diagonal elements of the Hamiltonian are just the exchange integrals:

$$H_{ij} = \left\langle \phi_i\phi_i \left| \frac{1}{r_{12}} \right| \phi_j\phi_j \right\rangle. \tag{45}$$

These have been shown to be non-negative and are zero only when $\phi_i(\vec{r})\phi_j(\vec{r}) = 0$ everywhere [7]. Adding an additional NO gives a Hamiltonian matrix of the form:

$$\begin{pmatrix} H & y \\ y^\dagger & h \end{pmatrix}. \tag{46}$$

The necessary condition for the additional NO to not contribute to lowering the energy is that $\boldsymbol{C}^\dagger \boldsymbol{y} = 0$. Here $\boldsymbol{C}$ is the vector of configuration coefficients for the n-term wavefunction and $y_i = \langle \phi_i \phi_i | 1/r_{12} | \phi_{n+1} \phi_{n+1} \rangle$. If this condition can not be met then there is a contradiction with the assumption that the n-term expansion is exact. Although it seems unlikely that $\boldsymbol{y}$ is orthogonal to $\boldsymbol{C}$ for any finite value of n, it has not thus far been proven.

7 Discussion

The completeness of the occupied NSO's (or NO's) depends on the nature of the electron-electron interaction. We have examined several exactly-soluble two-electron models to determine whether their occupied NO's form complete sets. The set of occupied NO's is not complete for model Hamiltonians which have no electron-electron interaction. The occupied NO's for the one-dimensional and the three-dimensional coupled harmonic oscillators form complete sets. The harmonic oscillators coupled with an inverse quadratic repulsion resulted in one-matrices which could be expressed in terms of finite, incomplete sets for some values of the coupling constant. For other values of the coupling constant it is probably true that the occupied NO's form complete sets. There are other exactly-soluble, two-electron models [8, 9], but they don't lend themselves to the exact analytical examination that the ones reported here do.

We have examined without rigorous proof the question of whether the occupied NO's for the helium atom form a complete set. A related question is the question of the exactness of the extended Koopmans' theorem (EKT) [10–14] ionization potentials. It has been shown for helium that if the occupied NO's form a complete set, then all of the EKT ionization potentials are exact [15]. Calculations of the lowest and several of the higher EKT ionization potentials for helium are very close to the exact ones [12], tantalizingly suggesting that the NO's with nonzero occupation numbers form a complete set. Based on this numerical evidence and on the, as yet unproven, formal arguments presented here, it is reasonable to conclude that the set of occupied NO's for the ^1S state of helium is complete for the Hamiltonian which includes the electron repulsion. The NO's of some states of He would not be complete because of symmetry restrictions. For example a two electron P state with gerade symmetry would have no s orbitals. We expect that the occupied NO's for many-electron atoms and molecules in fact form complete sets. A rigorous proof must depend on the special nature [16] of the Coulombic interaction of the electrons.

The preceding analysis eliminates the apparent disagreement between the proofs for the exactness and the inexactness of the extended Koopmans' theorem. The Katriel–Davidson proof for the exactness of the extended Koopmans' theorem depends explicitly on the electron-electron Coulomb repulsion [14]. The Pickup–Snijders perturbation-theory-based arguments, which indicate that the extended Koopmans' theorem is not in general exact [14], do not take into account the specific nature of the electron-electron potential; these arguments do not forbid the extended Koopmans' theorem from exactly applying to the specific Coulomb interaction case.

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