

Many-body Hamiltonian with screening parameter and ionization energy

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Abstract. We prove the existence of a Hamiltonian with ionization energy as part of the eigenvalue, which can be used to study strongly correlated matter. This eigenvalue consists of total energy at zero temperature (E_0) and the ionization energy (ξ). We show that the existence of this total energy eigenvalue, $E_0 \pm \xi$, does not violate the Coulombian atomic system. Since there is no equivalent known Hamilton operator that corresponds quantitatively to ξ , we employ the screened Coulomb potential operator (Yukawa-type), which is a function of this ionization energy to analytically calculate the screening parameter (σ) of a neutral helium atom in the ground state. In addition, we also show that the energy level splitting due to spin-orbit coupling is inversely proportional to ξ eigenvalue, which is also important in the field of spintronics.

Keywords. Yukawa-type potential; ionization and excitation energies; many-body Hamiltonian; spin-orbit coupling; energy-level splitting.

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1. Introduction

Finding even an approximate but an accurate solution to a Coulombian many-body problem (many-electron atoms and solids) is no doubt, one of the most important problems in physics [1]. The Rayleigh–Ritz variational (RRV) method [2] is a common and a powerful method regardless of the type of potential used (neglecting $e-e$ interaction) to solve a particular Hamiltonian [3]. In the presence of $e-e$ interaction, one can still use the RRV method, for example, in the presence of screened Coulomb potential (Yukawa-type) to calculate the total energy eigenvalue [4]. The Yukawa-type potential [5], $V = -(1/r) \exp[-\sigma r]$ is one of the well-studied potentials and the focus is usually on how to enumerate σ for a given bound state [6]. In this work however, we will define the screening parameter, σ , as a function that depends on the ionization potential [7], in which, we will treat σ as a many-body parameter in real atoms. On the other hand, there are also methods employed to tackle screening effect namely, renormalization group [8], $1/N$ expansion [9],

screened Coulomb potential in the momentum representation [10] and Dirac and Klein–Gordon equations with relativistic effects [11]. These methods, though very useful and accurate, do not allow one to associate the different isolated atomic energy levels for all the ions that exist in solids to changes in the electronic excitation probability in solids. This association is important to predict electronic properties of solids with different ions.

As such, we propose here a many-body Hamiltonian with ionization energy as its eigenvalue to study just that, using the Yukawa-type potential. One of the fundamental requirements from the electronic characterizations of materials is to understand what parameters effectively control the flow of electrons. Adding to that, all electrons are the same and indistinguishable. However, the energy that each electron or a group of electrons possess is different in different materials due to different types of atoms in a given material. This is also true for electrons in atoms due to different magnitudes of electron–nucleus Coulomb force. In view of this, this Hamiltonian interrogates the atomic ionization energy or the atomic energy-level difference to reveal information about the electronic energies. In other words, we can theoretically predict the systematic changes to the carrier density and conductivity with respect to different dopants in a given non-free electron compound. Such predictions are not only important for experimentalists to evaluate their data and design new materials, but also theoretically significant to understand what parameters influence the motion of electrons in strongly correlated matter. The eigenvalue of this Hamiltonian is made up of the total energy at zero temperature (E_0) and ionization energy (ξ). The total energy from this Hamiltonian has been verified in experiments where the isolated atomic energy levels have been used to predict the changes of the electronic excitation probability in solids (ref. [7] and references therein). Our motivation here is: (i) to give proofs-of-existence that the right-hand side (eigenvalue) and the left-hand side (Hamilton operator) of this many-body Hamiltonian are physically equivalent. We apply this Hamiltonian to hydrogen and helium atoms solely to justify (i). In order to do so, we will need to find an operator that corresponds to ξ eigenvalue and prove that it yields the same conclusion as ξ itself. We first establish the validity of this eigenvalue for the 1D systems and hydrogen atom. Secondly, we will show that the screened Coulomb potential (V_{sc}) is the operator that corresponds to ξ , and the screened Coulomb potential in atomic He is also proportional to the ionization energy. In addition, (ii) we also discuss the application of this Hamiltonian in the under-screened Kondo metal and (iii) we derive an expression that associates the spin-orbit coupling and the ionization energy, through the screener, σ , which is also important for solids. Our main results are inclined toward the application of our Hamiltonian to solids and we make use of the non-relativistic atomic properties of two-electron atom and ions to prove the validity of this Hamiltonian, as listed in (i), (ii) and (iii).

2. Many-body Hamiltonian as a function of ionization energy

The three-dimensional Schrödinger equation for fermions with mass m moving in the presence of potential $V(\mathbf{r})$ is given by (after making use of the linear momentum operator, $\hat{p} = -i\hbar\nabla^2$) [12].

Many-body Hamiltonian

$$-\frac{\hbar^2}{2m}\nabla^2\varphi = (E + V(\mathbf{r}))\varphi. \quad (1)$$

E denotes the total energy. We define,

$$\pm\xi := E_{\text{kin}} - E_0 + V(\mathbf{r}), \quad (2)$$

such that $\pm\xi$ is the energy needed for a particle to overcome the bound state and the potential that surrounds it. E_{kin} and E_0 denote the total energy at $V(\mathbf{r}) = 0$ and the energy at $T = 0$, respectively, i.e., E_{kin} = kinetic energy. In physical terms, ξ is defined as the ionization energy. That is, ξ is the energy needed to excite a particular electron to a finite r , not necessarily $r \rightarrow \infty$.

Proof. At $T = 0$ and $V(\mathbf{r}) = 0$, $\hat{H}\varphi = -(\hbar^2/2m)\nabla^2\varphi = E_0\varphi$. Hence, from eq. (1) with $V(\mathbf{r}) = 0$ and $T = 0$, the total energy can be written as

$$E = E_{\text{kin}} = E_0. \quad (3)$$

Remark 1. Therefore, for an electron to occupy a higher energy state N from the initial state M is more probable than from the initial state L if the condition, $[E_N(\geq 0) - E_M(\geq 0)] < [E_N(\geq 0) - E_L(\geq 0)]$ when certain T is satisfied. As for a hole to occupy a lower state M from the initial state N is more probable than to occupy a lower state L if the condition, $|E_M(< 0) - E_N(< 0)| < |E_L(< 0) - E_N(< 0)|$ at certain T is satisfied. On the other hand, using the above-stated new definition (eq. (2)) and the condition, $T = 0$, we can rewrite the total energy as

$$E = E_{\text{kin}} = E_0 \pm \xi. \quad (4)$$

Therefore, Remark 1 can be rewritten as Remark 2.

Remark 2. For an electron to occupy a higher energy state N from the initial state M is more probable than from the initial state L , if the condition, $\xi(M \rightarrow N) < \xi(L \rightarrow N)$ at certain T is satisfied. As for a hole to occupy a lower state M from the initial state N is more probable than to occupy a lower state L if the condition, $\xi(N \rightarrow M) < \xi(N \rightarrow L)$ at certain T is satisfied. For electron-like excitations, Remark 2 implies that $\xi(M \rightarrow N) = [E_N(\geq 0) - E_M(\geq 0)]$, $\xi(L \rightarrow N) = [E_N(\geq 0) - E_L(\geq 0)]$, while $\xi(N \rightarrow M) = |E_M(< 0) - E_N(< 0)|$, $\xi(N \rightarrow L) = |E_L(< 0) - E_N(< 0)|$, for hole-like excitations. In other words, if we let the energy function, $E = E_0 \pm \xi = E_{\text{kin}} + V(\mathbf{r})$, then we can write the many-electron atomic Hamiltonian as

$$\hat{H}\varphi = (E_0 \pm \xi)\varphi. \quad (5)$$

In the subsequent sections, we will first apply eq. (5) to well-known systems in order to have a clearer picture, before applying it to the under-screened Kondo metal (our choice of strongly correlated matter).

Infinite square-well potential. Since the early days of quantum mechanics, the total energy of a given system was neither introduced nor proven in the form of $E_0 \pm \xi$.

In addition, eq. (5) is still in its infancy and therefore, we need to re-examine its accuracy by first applying it to simple systems. Here, the Hamiltonian given in eq. (5) is applied to a free electron system, by considering a free-particle of mass m moving in one dimension of an infinite square well (width = a). Therefore, eq. (5) can be solved generally, to give $\varphi_n = C \sin[((2m/\hbar^2)(E_0 \pm \xi))^{1/2} x]$. After normalization, $\int_0^a |C|^2 \sin^2[((2m/\hbar^2)(E_0 \pm \xi))^{1/2} x] dx = |C|^2 a/2 = 1$, one obtains $C = \sqrt{2/a}$. Finally, the normalized wave function $\varphi_n = \sqrt{(2/a)} \sin[((2m/\hbar^2)(E_0 \pm \xi))^{1/2} x]$. Applying the boundary conditions for free electrons $V(x) = 0$; $\xi = E_{\text{kin}} - E_0 + [V(x) = 0] = E_{\text{kin}} - E_0$; $E = E_0 \pm \xi$, $\varphi(0) = 0$ and $\varphi(a) = 0$ require $((2m/\hbar^2)(E_0 \pm \xi))^{1/2} = n\pi/a$. Note here that the condition $V(x) = 0$ that leads to the free-electron concept also implies that the square well potential equals zero anywhere between 0 and a ($0 < x < a$), and this will stay true for as long as $a \gg 2r_e$ where r_e denotes an electron's radius. Eventually, one arrives at

$$\varphi_n = \sqrt{\frac{2}{a}} \sin \left[\frac{n\pi}{a} x \right]. \quad (6)$$

Obviously, one can also obtain the exact form of eq. (6) from the 1D time-independent Schrödinger equation with $V(x) = 0$ and $k_n = n\pi/a$ (ref. [13]). Therefore, we can conclude that our Hamiltonian is exactly the same as the usual Hamiltonian. However, in the presence of potential energy, our Hamiltonian will provide additional information on the energetics of fermions in different atoms. This new information will tell us how one can use the atomic energy level difference to predict the electronic excitation probability in solids via Fermi-Dirac statistics [7].

1D Dirac-delta potential: As a matter of fact, there can be many general solutions for eq. (5) with $V(x) \neq 0$ and these solutions can be derived in such a way that they can be compared, term by term, with the known wave functions. For example, if $V(x) = -\alpha\delta(x)$, then we need a solution in the form of $\varphi(x) = C \exp[-iax]$ and the associated wave function can be derived as $\partial\varphi(x)/\partial x = -iaC \exp[-iax]$, $\partial^2\varphi(x)/\partial x^2 = -a^2\varphi(x)$. We can rewrite eq. (5) to get

$$\frac{\partial^2\varphi}{\partial x^2} = -\frac{2m}{\hbar^2}[E_0 \pm \xi]\varphi. \quad (7)$$

Using eq. (7), we find $a = [(2m/\hbar^2)(E_0 \pm \xi)]^{1/2}$. Therefore, $\varphi(x) = C \exp[-i((2m/\hbar^2)(E_0 \pm \xi))^{1/2} x]$. Normalizing φ gives $1 = \int_{-\infty}^{+\infty} |\varphi(x)|^2 dx = C^2/[i((2m/\hbar^2)(E_0 \pm \xi))^{1/2}]$. Hence,

$$\varphi(x) = i^{1/2} \left[\frac{2m}{\hbar^2} (E_0 \pm \xi) \right]^{1/4} \exp \left[-i \left(\frac{2m}{\hbar^2} (E_0 \pm \xi) \right)^{1/2} x \right]. \quad (8)$$

Term by term comparison between eq. (8) and [13] $\varphi(x) = (m\alpha/\hbar) \exp[-m\alpha|x|/\hbar^2]$, gives the bound state energy, $E_0 \pm \xi = -m\alpha^2/2\hbar^2$ by equating either $[i^2((2m/\hbar^2)(E_0 \pm \xi))]^{1/4} = m\alpha/\hbar$ or $-i((2m/\hbar^2)(E_0 \pm \xi))^{1/2} x = -m\alpha|x|/\hbar^2$.

3. Hydrogen atom

In this section, eq. (5) is applied to a hydrogen atom with Coulomb potential and subsequently, exact results of its energy levels are derived. The following derivations are important to prove that the total energy $E_0 \pm \xi$ given in eq. (5) is also exact and ξ is not a correction term. The radial equation of a hydrogen atom is given by [13]

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu. \quad (9)$$

Equation (9) can be rewritten using $E = E_0 \pm \xi$ and can be readily solved [13] to obtain the principal quantum number n

$$2n = \frac{me^2}{2\pi\epsilon_0\hbar^2 \sqrt{\frac{2m}{\hbar^2}(E_0 \pm \xi)}}, \quad \therefore \sqrt{\frac{2m}{\hbar^2}(E_0 \pm \xi)} = \left[\frac{me^2}{4\pi\epsilon_0\hbar^2} \right] \frac{1}{n} = \frac{1}{a_B n}. \quad (10)$$

a_B denotes the Bohr radius and ϵ_0 is the permittivity of space. m and \hbar are the particle's mass and the Planck constant, respectively. Equation (10) can be rewritten so as to obtain the energy levels of a hydrogen atom as

$$(E_0 \pm \xi)_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = E_n. \quad (11)$$

We propose that $(E_0 \pm \xi)_n$ can be rewritten in terms of the standard E_n where, $-(E_0 \pm \xi)_n = -E_n$.

Proof.

$$\begin{aligned} -(E_0 \pm \xi)_{m+1} &= -[E_0 \pm (E_m - E_{m+1})] \Leftrightarrow \text{eq. (2)} \\ &= -[E_m \pm (E_m - E_{m+1})] \Leftrightarrow E_0 = E_m = \text{ground state} \\ &= -[E_m - E_m + E_{m+1}] \Leftrightarrow E_m < E_{m+1} \quad \therefore \pm \rightarrow - \\ &= -E_m + E_m - E_{m+1} = -E_{m+1}. \end{aligned} \quad (12)$$

Alternatively, one can also show that

$$\begin{aligned} -(E_0 \pm \xi)_{m+1} &= -[E_0 \pm (E_{m+1} - E_m)] \Leftrightarrow \text{eq. (2)} \\ &= -[E_m \pm (E_{m+1} - E_m)] \Leftrightarrow E_0 = E_m = \text{ground state} \\ &= -[E_m + E_{m+1} - E_m] \Leftrightarrow E_{m+1} > E_m \quad \therefore \pm \rightarrow + \\ &= -E_m + E_m - E_{m+1} = -E_{m+1}. \end{aligned} \quad (13)$$

Equation (12) or (13) can be used to calculate $(E_0 \pm \xi)_n$. Example:

$$\begin{aligned} -(E_0 \pm \xi)_{n=1} &= -[E_0 \pm (E_{n=1} - E_{n=1})] = -E_{n=1} \\ -(E_0 \pm \xi)_{n=2} &= -[E_{n=1} - (E_{n=1} - E_{n=2})] = -E_{n=2} \\ -(E_0 \pm \xi)_{n=3} &= -[E_{n=1} - (E_{n=1} - E_{n=3})] = -E_{n=3} \\ &\dots \end{aligned} \quad (14)$$

Consequently, energy levels for a hydrogen atom can be written exactly, either as $(E_0 \pm \xi)_n$ or as E_n . Alternatively, we can also assume a solution for the hydrogen atom in the form of $\varphi_{n=1,l=0,m=0}(r, b) = C \exp[-br^2]$ comparable with [13] the standard hydrogenic radial wave function,

$$\varphi_{100}(r, \theta, \varphi) = \frac{1}{\sqrt{\pi a_B^3}} e^{-r/a_B}. \quad (15)$$

Therefore, we obtain $\ln \varphi(r) = \ln C - br \ln e$, $(1/\varphi(r))(\partial\varphi(r)/\partial r) = -b$ and $(\partial^2\varphi(r)/\partial r^2) = -b(\varphi(r)/\varphi(r))$. Equation (7) is used to obtain

$$b = \frac{i}{\hbar} \sqrt{2m[E_0 \pm \xi]}. \quad (16)$$

Normalization requires $1 = \int_{-\infty}^{+\infty} |\varphi(r)|^2 d^3\mathbf{r} = 4\pi C^2 (2!/(2b)^3)$, and consequently, $\varphi_{100}(r, b) = \sqrt{(b^3/\pi)} \exp[-br]$ and $b = 1/a_B$. The expectation value of the momentum can be calculated as, $\langle p \rangle = \int_{-\infty}^{+\infty} \varphi(r, b) (-i\hbar(\partial/\partial r)) \varphi(r, b) d^3\mathbf{r} = \hbar/ia_B$. The momentum can also be written as, $p = \hbar^2 k^2 = \sqrt{2m(E_0 \pm \xi)}$, and hence

$$a_B = \frac{\hbar}{i} \sqrt{\frac{1}{2m(E_0 \pm \xi)}}, \quad \therefore E_0 \pm \xi = -\frac{\hbar^2}{2ma_B^2} = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = E_1. \quad (17)$$

Note that eq. (17) can also be obtained from eq. (16). Equation (17) is the ground state energy for atomic hydrogen, as it should be and it justifies the applicability of eq. (5). Now, for free many-electron atoms, it is necessary to invoke eqs. (12)–(14) which can be easily extended exactly to free many-electron atoms. For example, the eigenvalue for the atomic Mn with electronic configuration, $[\text{Ar}]3d^5 4s^2$ can be written as (after exciting one of the $4s^2$ electron to $4p$)

$$\begin{aligned} -(E_0 \pm \xi)_{4p^1} &= -[E_0 \pm (E_{4p^1} - E_{4s^2})] \Leftrightarrow \text{eq. (2)} \\ &= -[E_{4s^2} \pm (E_{4p^1} - E_{4s^2})] \Leftrightarrow E_0 = E_{4s^2} = \text{initial state} \\ &= -[E_{4s^2} + E_{4p^1} - E_{4s^2}] \Leftrightarrow E_{4p^1} > E_{4s^2} \quad \therefore \pm \rightarrow + \\ &= -E_{4p^1}. \end{aligned} \quad (18)$$

Using eq. (2), one can also write $\xi = E_{\text{kin}} - E_0 + V(x) = E_{4p^1} - E_{4s^2}$, which suggests that we can describe the excited electron's properties from the energy level difference, before and after the excitation. All the results presented here, thus far are exact and straightforward. Importantly, recall that our motivation here is to show eq. (5) is exact for atomic hydrogen as well as for many-electron atoms (eq. (18)). The reason it is also exact for many-electron atoms is due to our definition of ξ , which can be obtained from a given atomic spectrum. The price we pay is that we are unable to determine the real wave function from eq. (5). In the following section, our objective is to understand theoretically the implications of ξ on the operator side, because we need to prove that the left-hand side (LHS) of eq. (5) is also physically correct compared to its RHS. Unfortunately, we will have to show this at the expense of accuracy. In other words, we cannot calculate the complete relativistic and radiation effects of atoms using our proof. However, this lack of accuracy does not invalidate our objective, as stated above.

4. Screened Coulomb potential and helium atom

In the previous sections, we only worked on the RHS of the Hamiltonian, eq. (5), which is the total energy eigenvalue and we did not touch the Hamilton operator (LHS). In the subsequent sections however, we will need to solve the Hamilton operator in order to evaluate the influence of the ionization energy on the operator side (LHS). Of course, we cannot expect to find an isolated or a stand-alone operator that could correspond quantitatively to the ionization energy eigenvalue on the RHS. This is true for all atoms with potential energy attached, including the electron–electron ($e-e$) interaction term that gives rise to screening. Mathematically, we say that this one(LHS)-to-one(RHS) ($V_{sc}(\mathbf{r})$ to ξ) correspondence does not exist because ξ has been defined as a function of both kinetic and potential energies (see eq. (2)). However, we can repackage the Coulombian $e-e$ repulsion potentials as the screened Coulomb potential (Yukawa-type) for atoms other than hydrogen. Therefore, we can use the screened Coulomb potential to evaluate how the ionization energy influences the screened Coulomb potential in atomic He. Before we move on, let us just accentuate an important point here. Indeed, it is true that common techniques of many-body theory require handling of the Hamilton operator first, and then calculate the corresponding eigenvalue (E , the total energy). In this paper however, we are doing just the opposite, meaning, we have redefined the total energy eigenvalue, as given in eq. (5), and now we are in the midst of verifying its consequences on the Hamilton operator. Of course, this verification is indirect simply because we do not have a stand-alone operator that quantitatively corresponds to the eigenvalue, ξ . As such, we will make use of the screened Coulomb potential operator, which is given by [7]

$$\hat{V}_{sc} = \frac{e}{4\pi\epsilon_0 r} e^{-\mu r e^{\frac{1}{2}\lambda(-\xi)}} = \frac{e}{4\pi\epsilon_0 r} e^{-\sigma r}. \quad (19)$$

Here, μ is the screener's constant of proportionality, while $\lambda = (12\pi\epsilon_0/e^2)a_B$. All we have to do now is to show that for atomic He, $\langle \hat{V} \rangle_{sc}$ is inversely proportional to σ . Secondly, we will also need to show that $\langle \hat{V} \rangle_{sc}$ is proportional to the ionization energy, by comparing with other two-electron systems. For example, when we compare atomic He with other two-electron ions, namely, Li^+ and Be^{2+} , then we expect $\langle \hat{V} \rangle_{sc}^{\text{He}} < \langle \hat{V} \rangle_{sc}^{\text{Li}^+} < \langle \hat{V} \rangle_{sc}^{\text{Be}^{2+}}$, because $\xi_{\text{He}}(54.4 - 24.6 = 29.8 \text{ eV}) < \xi_{\text{Li}^+}(122.5 - 73.6 = 46.8 \text{ eV}) < \xi_{\text{Be}^{2+}}(217.7 - 153.9 = 63.8 \text{ eV})$.

Helium atom: Here, we will first find the expectation value for the screened Coulomb potential for atomic He. Recall that our intention here is to justify ξ on the operator side via the screened Coulomb potential (eq. (19)). The He wave function is the product of two hydrogenic wave functions (recall that we are not solving the Hamiltonian for the He atom, rather we are only solving the screened Coulomb potential operator) [12],

$$\varphi_0(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{100}(\mathbf{r}_1)\varphi_{100}(\mathbf{r}_2) = \frac{Z^3}{a_B^3\pi} e^{-Z(r_1+r_2)/a_B}. \quad (20)$$

Subsequently, the mutual screening between the electrons, \mathbf{r}_1 and \mathbf{r}_2 , implies that both electrons have identical effective charge of $<2e$ because they screen each other. Hence,

$$\begin{aligned} \langle \hat{V} \rangle_{\text{sc}} &= \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z^3}{a_B^3\pi} \right]^2 \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-2Z(r_1+r_2)/a_B} e^{-\sigma(r_1+r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\ &= \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2a_B} \right) \frac{40Z^6}{(2Z + a_B\sigma)^5} = \frac{40Z^6 E_1}{[2Z + a_B\sigma]^5}, \end{aligned} \quad (21)$$

where $|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos(\theta_2)}$. From eq. (21), it is clear that σ is inversely proportional to the ionization energy, whereas the screened Coulomb potential is proportional to the ionization energy. The complete Hamiltonian for the helium atom can be written as (with the screened Coulomb potential as the correction term, ignoring fine structure and other corrections)

$$\hat{H} = \hat{H}_o + \hat{V}_{\text{sc}}, \quad (22)$$

where \hat{H}_o is given by [12,13]

$$\hat{H}_o = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left[\frac{2}{r_1} + \frac{2}{r_2} \right]. \quad (23)$$

In eq. (22), we again simplified the Hamilton operator by strictly forcing the $e-e$ interaction into the $\langle \hat{V} \rangle_{\text{sc}}$ as the correction term. Therefore, the non-relativistic many-body Hamiltonian (again, ignoring the fine structure corrections) can now be written as

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \left[\frac{Z}{r_i} - \frac{1}{2} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} e^{-\sigma(r_i+r_j)} \right], \quad (24)$$

while its eigenvalue is exactly equal to $E_0 \pm \xi$. Firstly, the aim of eq. (24) is to point out that the eigenvalue, ξ and $\langle \hat{V} \rangle_{\text{sc}}$ provide the same conclusions. Secondly, one can use the ionization energy to make certain quantitative and qualitative predictions in solids via eq. (5) and qualitatively in atoms (eq. (24)). Apparently, eq. (24) is only suitable to evaluate the non-relativistic atomic properties and the spin-orbit coupling qualitatively. As a consequence, eq. (24) is not suitable to evaluate the atomic energy levels accurately with respect to relativistic and radiation corrections. The total-energy expectation value for atomic He can be obtained (as given below) by using eq. (24),

$$\langle \hat{H} \rangle = 8E_1 + \langle \hat{V} \rangle_{\text{sc}}. \quad (25)$$

Note here that eq. (25) is mathematically identical to eq. (5), where $E_0 \pm \xi = 8E_1 + \langle \hat{V} \rangle_{\text{sc}}$ and ξ physically corresponds to $\langle \hat{V} \rangle_{\text{sc}}$ through the screener σ as defined earlier. Our problem now is to solve eq. (25), which is given by

$$\langle \hat{H} \rangle = 8E_1 + \frac{40Z^6 E_1}{[2Z + a_B\sigma_{\text{He}}]^5}. \quad (26)$$

Equation (26) tells us that with increased ionization energy (ξ), the magnitude of the screener (σ) is reduced and eventually, gives rise to stronger e - e interaction, $\langle \hat{V} \rangle_{\text{sc}}$. This conclusion is understandable because small ξ implies weak Coulomb force between the valence electron and the atomic core electrons, which in turn gives a strongly screened valence electron. As a consequence, this particular valence electron interacts less with the core electrons and defines the limit between the strongly correlated electrons ($\xi \rightarrow \infty$) and free-electron solids ($\xi \rightarrow 0$). Using the RRV method, one can capture the exact scenario stated above with variationally determined charge strength, $Z e < 2e$ for He atom [12,13]. Z is the atomic number. Since the ground state energy of the neutral He and H are known [14], 79.005 eV and 13.600 eV, we can estimate the screener for atomic He as

$$\sigma_{\text{He}} = \frac{1}{a_{\text{B}}} \left[\left(\frac{40(2^6)E_1}{-79.005 + 8E_1} \right)^{1/5} - 4 \right] = 2.02 \times 10^9 \text{ m}^{-1}. \quad (27)$$

The limit, $\lim_{\xi \rightarrow \infty} \langle \hat{V} \rangle_{\text{sc}} = \lim_{\sigma \rightarrow 0} \langle \hat{V} \rangle_{\text{sc}} = 34 \text{ eV}$, is purely due to electron-electron interaction (stronger) with zero screening. This value agrees exactly with the one calculated in ref. [13], also without screening. As a consequence, the ionization energy theory does not violate the true physical picture of the atomic He, both quantitatively and qualitatively. Now, let us calculate the screened Coulomb potential for other two-electron ions, namely, Li^+ and Be^{2+} . Using eq. (21), in the limit $\sigma \rightarrow 0$, we obtain $\langle \hat{V} \rangle_{\text{sc}}^{\text{Li}^+} = 51 \text{ eV}$ and $\langle \hat{V} \rangle_{\text{sc}}^{\text{Be}^{2+}} = 68 \text{ eV}$. Hence, we have $\langle \hat{V} \rangle_{\text{sc}}^{\text{He}} (34 \text{ eV}) < \langle \hat{V} \rangle_{\text{sc}}^{\text{Li}^+} (51 \text{ eV}) < \langle \hat{V} \rangle_{\text{sc}}^{\text{Be}^{2+}} (68 \text{ eV})$, as expected. Furthermore, we can crosscheck whether eq. (26) is derived without mistakes by showing that it satisfies the Hellmann-Feynman theorem [15],

$$\begin{aligned} \frac{\partial \langle \hat{H} \rangle}{\partial \sigma} &= \left\langle \varphi_0 \left| \frac{\partial \hat{H}}{\partial \sigma} \right| \varphi_0 \right\rangle \\ 40Z^6 E_1 \frac{\partial}{\partial \sigma} \left[\frac{1}{(2Z + a_{\text{B}}\sigma)^5} \right] &= \frac{e^2}{4\pi\epsilon_0} \left\langle \varphi_0 \left| \frac{\partial}{\partial \sigma} \left(\frac{e^{-\sigma(r_1+r_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \right| \varphi_0 \right\rangle \\ &= -\frac{200Z^6 E_1 a_{\text{B}}}{(2Z + a_{\text{B}}\sigma)^6}. \end{aligned} \quad (28)$$

In summary, we have justified the influence of the ionization energy in eq. (5) through the screeners and the screened Coulomb potential on the operator side, applied to the helium atom via eq. (24). In other words, the Hamilton operator with the screened Coulomb potential (Yukawa-type) has been used to prove the validity of ξ in the operator side, which also physically satisfies the RHS.

Application I (Under-screened Kondo metal): Let us now apply the total energy from eq. (5) to a recently reported under-screened Kondo metal. The Kondo effect is well established in magnetic ion-doped free-electron metals in which, the resistivity curve shifts upward with respect to magnetic ion content [16]. In addition, Sengupta and Baskaran [17] have also theoretically predicted the Kondo effect in graphene by changing the applied gate voltage. Even though eq. (5) cannot be

applied to free-electron metals [18], including the magnetic ion-doped free-electron metal, it can be used for under-screened Kondo metal. For example, Manyala *et al* [19] have employed various experimental techniques to measure the electronic properties, such as the electrical conductivity, magnetic susceptibility and specific heat of Mn-doped FeSi compound, and yet, it is not possible to pin-point directly the reasons why and how systematic increment of Mn content (from $x = 0.01$ to 0.025) increased the conductivity (below 5 K) of $\text{Fe}_{1-x}\text{Mn}_x\text{Si}$. They found that the regime below 5 K is due to under-screened Kondo effect. Furthermore, Manyala *et al* have indirectly explained the conductivity increment in this regime with Mn content as due to increment of temperature-independent mobile carriers. The increment of mobile carriers is assumed from the magnetic susceptibility (χ) results, where $\chi(T)$ curve shifts upward with x ($\chi \propto x$). Here, we give detailed explanations as to why Mn content gives rise to the conductivity. Knowing the fact that ξ is unique for each atom, we can employ the total energy ($E_0 \pm \xi$) as one of the restrictive condition to derive the ionization energy-based Fermi–Dirac statistics (*i*FDS). The respective distribution functions for electron and hole are given by [7]

$$f_e(E_0, \xi) = \frac{1}{e^{[(E_0+\xi)-E_F^{(0)}]/k_B T} + 1}; \quad f_h(E_0, \xi) = \frac{1}{e^{[E_F^{(0)}-(E_0-\xi)]/k_B T} + 1}, \quad (29)$$

where, for solids, $E_F^{(0)}$ is the Fermi level at $T = 0$, T and k_B are the temperature and Boltzmann constant, respectively. Note that the standard FDS and *i*FDS are theoretically exact, with non-trivial transformation between them. Let us pause here and derive this transformation so that we will not be bogged down with confusion and ambiguity at a later stage. Firstly, the three-dimensional density of states (DOS) is given by, $dn = (2m/\hbar^2)^{3/2}(VE_0^{1/2}/2\pi^2)dE_0$, V is the volume in \mathbf{k} -space and the carrier density (electrons) can be obtained from

$$\begin{aligned} n &= \int_0^\infty f_e(E_0, \xi) \frac{dn}{dE_0} dE_0 = \frac{V}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} e^{(E_F^{(0)}-\xi)/k_B T} \\ &\quad \times \int_0^\infty E_0^{1/2} \exp \left[-\frac{E_0}{k_B T} \right] dE_0 \\ &= 2V \left(\frac{k_B T m_e}{2\pi \hbar^2} \right)^{3/2} \exp \left[\frac{E_F^{(0)} - \xi}{k_B T} \right]. \end{aligned} \quad (30)$$

After comparing *i*FDS (eq. (29)) with standard FDS, we can see that $E_F(\text{FDS}) = E_F$ while for *i*FDS, $E_F(\text{iFDS}) = E_F^{(0)} + \xi$. Thus, in standard FDS, E_F needs to be varied accordingly with doping for a given temperature. *i*FDS on the other hand, captures the same variation due to doping with ξ in which, E_F^0 is fixed to be a constant (independent of T and doping). That is, E_F^0 is the Fermi level at $T = 0$, for a given compound. Now, let us write the total energy as (using eqs (5) and (30), also after taking $e^{[(E_0+\xi)-E_F^{(0)}]/k_B T} \gg 1$)

$$E_{i\text{FDS}} = (E_0 \pm \xi)n = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} e^{(E_F^{(0)}-\xi)/k_B T}$$

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$$\begin{aligned}
 & \times \int_0^\infty (E_0 \pm \xi) E_0^{1/2} e^{-E_0/k_B T} dE_0 \\
 &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} e^{(E_F^{(0)} - \xi)/k_B T} \int_0^\infty (E_0^{3/2} \pm \xi E_0^{1/2}) e^{-E_0/k_B T} dE_0 \\
 &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} e^{(E_F^{(0)} - \xi)/k_B T} \left[\frac{3}{4} \sqrt{\pi(k_B T)^5} \pm \frac{\xi}{2} \sqrt{\pi(k_B T)^3} \right]. \quad (31)
 \end{aligned}$$

Using eq. (30), eq. (31) simplifies to

$$E_{i\text{FDS}} = \frac{3n(E_F^{(0)}, \xi)}{2} k_B T \pm n(E_F^{(0)}, \xi) \xi. \quad (32)$$

Equation (32) must be transformed with $E_{i\text{FDS}} \rightarrow E_{\text{FDS}}$ and $(E_F^{(0)} + \xi) \rightarrow E_F$ in order to arrive at the classical system

$$E_{\text{FDS}} = \frac{3n(E_F)}{2} k_B T. \quad (33)$$

Importantly, eq. (33) can be reverse-transformed to eq. (32) or vice versa as given below ($E_{i\text{FDS}} \leftrightarrow E_{\text{FDS}}$ and $(E_F^{(0)} + \xi) \leftrightarrow E_F$)

$$\frac{3n(E_F)}{2} k_B T \leftrightarrow \frac{3n(E_F^{(0)}, \xi)}{2} k_B T \pm n(E_F^{(0)}, \xi) \xi. \quad (34)$$

Hence, eqs (33) and (34) show the required transformation between *i*FDS and the standard FDS. Note here that the above transformation can be understood as a change of variable, without any approximation in which $E_{i\text{FDS}} = E_{\text{FDS}}$. Thus far, we have shown that the explicit content of the Hamilton operator (\hat{H}), namely, the kinetic and potential energy operators need not be known explicitly since ξ is unique for each atom, which can be obtained from the experimental atomic spectra. As such, using eq. (29), one can actually estimate the excitation probability of electrons from different atoms in a given compound. For example, the total energy from eq. (5) carries the fingerprint of each constituent atom in a compound since this total energy is a function of the difference in the energy levels of each atom. Hence, the newly defined total energy preserves the atomic level electronic fingerprint in the compound. In non-free electronic solids, ξ implies the energy needed to excite an electron to a finite distance, r , not $r \rightarrow \infty$. In solids, the magnitude of ξ is exactly what we need to know that reasonably defines the electronic properties. Subsequently, we make use of the *i*FDS to calculate the carrier density (eq. (30)). Now, for qualitative predictions, we can write $\xi = E_I^{\text{real}} \propto E_I$, where E_I is the ionization energy of a free atom or ion (with $r \rightarrow \infty$), and its average value can be obtained from [18,20]

$$E_I = \sum_i^z \frac{E_{Ii}}{z}. \quad (35)$$

The subscript $i = 1, 2, \dots, z$, where z denotes the number of valence electrons that can be excited or that can contribute to the electronic properties of a solid. In

order to obtain quantitative prediction, we need to know ξ . Hence, all we need to know now is the relationship between E_I and x . Since Mn-doped FeSi is equivalent to hole doping [19], we can surmise that the average valence state of Mn should be less than Fe. Thus, using eq. (35) we obtained the respective averaged values for the ionization energies, $E_I(\text{Mn}^{2+,3+} = 1113.1, 1824.8 \text{ kJ mol}^{-1}) < E_I(\text{Fe}^{3+,4+} = 1760.5, 2642.9 \text{ kJ mol}^{-1})$. Prior to averaging, the ionization energies for Mn and Fe elements were taken from ref. [21]. Smaller E_I gives rise to large carrier density and conductivity. However, this scenario is reversed if E_I is large. Consequently, Mn content (with smaller E_I) systematically decreases the E_I of the compound and subsequently increases the carrier density. This in turn shifts the T -dependent conductivity (below 5 K) curves upward with respect to Mn doping in $\text{Fe}_{1-x}\text{Mn}_x\text{Si}$, due to eq. (30). In principle, we can use this theory to fine-tune the conductivity in the under-screened Kondo regime of $\text{Fe}_{1-x}\text{Mn}_x\text{Si}$ with elements other than Mn.

5. Energy level splitting due to spin-orbit coupling

In this section, our intention is to find a qualitative expression between the spin-orbit splitting and the ionization energy. As pointed out earlier, this calculation also does not take into account the complete relativistic and radiation effects. The spin-orbit coupling operator after incorporating the screened Coulomb potential (eq. (19)) is given by

$$\hat{H}_{\text{SOC}} = \frac{\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \left\{ \frac{1}{r} \frac{d}{dr} \frac{1}{r} e^{-\mu r e^{\frac{1}{2}\lambda(-\xi)}} \right\} = \hat{\mathbf{D}} \left\{ \frac{\sigma e^{-\sigma r}}{r^2} + \frac{e^{-\sigma r}}{r^3} \right\}, \quad (36)$$

where [22]

$$\langle \hat{\mathbf{D}} \rangle = \frac{Ze^2\hbar^2}{16m^2c^2\pi\epsilon_0} (l, -l-1), \quad (37)$$

c is the speed of light, $\hat{\mathbf{S}}$ and $\hat{\mathbf{L}}$ are the spin and orbital angular momentum operators, respectively. The l in $(l, -l-1)$ is for $j = l + \frac{1}{2}$, while the $-l-1$ is for $j = l - \frac{1}{2}$. We ignore the irrelevant part of the Hamiltonian for the time being (labelled $\hat{\mathbf{D}}$) and focus on the term in the curly bracket. Here we consider the hydrogenic wave function again, given by [12]

$$\varphi_{210}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{32\pi} \left(\frac{Z}{a_B} \right)^5 r_1 r_2 e^{(-Z/a_B)(r_1+r_2)} \cos\theta_1 \cos\theta_2. \quad (38)$$

Recall here that we can use the appropriate hydrogenic wave function, depending on the type of orbital, since our corrections have been incorporated into the screened Coulomb potential (see eq. (25)). From eq. (36) we have

$$\langle \hat{H} \rangle_{\text{SOC}} = \langle \hat{\mathbf{D}} \rangle \left[\left\langle \varphi_{210} \left| \frac{\sigma e^{-\sigma r}}{r^2} \right| \varphi_{210} \right\rangle + \left\langle \varphi_{210} \left| \frac{e^{-\sigma r}}{r^3} \right| \varphi_{210} \right\rangle \right]. \quad (39)$$

We solve the two potential terms separately,

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$$\begin{aligned}
 \langle \hat{\mathbf{D}} \rangle \cdot \left\langle \varphi_{210} \left| \frac{\sigma e^{-\sigma r}}{r^2} \right| \varphi_{210} \right\rangle &= \langle \hat{\mathbf{D}} \rangle \frac{\sigma}{(32\pi)^2} \left(\frac{Z}{a_B} \right)^{10} \\
 &\times \int r_1^2 e^{-(Z/a_B)r_1} \cos^2 \theta_1 d^3 \mathbf{r}_1 \int r_2^2 \frac{e^{-[(Z/a_B)+\sigma]r_2}}{r_2^2} \cos^2 \theta_2 d^3 \mathbf{r}_2 \\
 &= \langle \hat{\mathbf{D}} \rangle \left(\frac{Z}{a_B} \right)^5 \frac{\sigma a_B^3}{12(\sigma a_B + Z)^3}, \tag{40}
 \end{aligned}$$

and

$$\langle \hat{\mathbf{D}} \rangle \cdot \left\langle \varphi_{210} \left| \frac{e^{-\sigma r}}{r^3} \right| \varphi_{210} \right\rangle = \langle \hat{\mathbf{D}} \rangle \left(\frac{Z}{a_B} \right)^5 \frac{a_B^2}{24(\sigma a_B + Z)^2}.$$

Finally,

$$\langle \hat{H} \rangle_{\text{SOC}} = \langle \hat{\mathbf{D}} \rangle \left(\frac{Z}{a_B} \right)^5 \left[\frac{\sigma a_B^3}{12(\sigma a_B + Z)^3} + \frac{a_B^2}{24(\sigma a_B + Z)^2} \right]. \tag{41}$$

Apart from $\langle \hat{V} \rangle_{\text{sc}}$, we also find that the spin-orbit separation \hat{H}_{SOC} is proportional to ξ . \hat{H}_{SOC} also satisfies the Hellmann–Feynman theorem,

$$\frac{\partial \langle \hat{H} \rangle_{\text{SOC}}}{\partial \sigma} = \left\langle \varphi_{210} \left| \frac{\partial \hat{H}_{\text{SOC}}}{\partial \sigma} \right| \varphi_{210} \right\rangle = -\langle \hat{\mathbf{D}} \rangle \frac{\sigma a_B^4}{4(\sigma a_B + Z)^4} \left(\frac{Z}{a_B} \right)^5. \tag{42}$$

Using the value for screener calculated earlier ($2 \times 10^9 \text{ m}^{-1}$), we find a crude estimate for the spin-orbit separation for He in 2p orbital, which is given by

$$\delta \langle \hat{H} \rangle_{\text{SOC}} = 3.9 \times 10^{-6} (l, -l - 1) \text{ eV} = 0.72 \text{ meV} \Leftrightarrow l = 1. \tag{43}$$

This calculated value is reasonable compared to the relativistic corrections [14] for 1s orbital ($l = 0$), which is 0.00311 eV. Apparently, $\delta \langle \hat{H} \rangle_{\text{SOC}}$ will be smaller even for $l = 1$ as a result of relativistic kinetic energy exclusion, because relativistic correction for $l = 1$ must come from both spin-orbit coupling and relativistic kinetic energy [12].

Application II (many-electron atoms): There is one important relationship, given in eq. (41) that we can use to qualitatively check the energy level splitting in many-electron atoms. Equation (41) says that the magnitude of the energy level splitting (δ), of a particular orbital is proportional to the energy level difference (ξ), of two different orbitals. That is, if the energy level difference is large, then it implies that δ is also large. δ and ξ can be compared to the experimental atomic spectra using the following approximate formulae:

$$\xi = {}^y E_L^{\text{max}} - {}^x E_L^{\text{min}}, \tag{44}$$

$$\delta = {}^x E_L^{\text{max}} - {}^x E_L^{\text{min}}, \tag{45}$$

where x and y denote the different electronic configuration (EC) and/or spectroscopic term. That is, for atomic He, $x = 1s3p: {}^3P$ and $y = 1s3d: {}^3D$, for atomic C,

$x = 2s^2 2p^2: ^3P$ and $y = 2s^2 2p^2: ^1D$, and so on. The magnitude of ξ and δ can be calculated for atomic Mn using eqs (44) and (45): $^y E_L^{\max} = 2.319170$ eV, $^x E_L^{\min} = 2.114214$ eV, therefore $\xi = 2.319170 - 2.114214 = 204.96$ meV, whereas, $^x E_L^{\max} = 2.186728$ eV thus, $\delta = 2.186728 - 2.114214 = 72.51$ meV. Here, three atomic spectra namely, He-I, C-I and Mn-I, as representatives of the periodic table are considered and are available in ref. [23]. However, there are also atoms where the energy level difference is not clearly defined because of the energy-level overlapping and incomplete spectroscopic data (for example, atomic Nd-I). The selected electronic configuration (EC), J (total angular momentum), spectroscopic term (ξ), energy levels (E_L) and its splittings (δ) are listed in table 1. It is clear from table 1 that the ionization energy concept invoked in the many-body Hamiltonian (see eqs (5) and (24)) explains the energy level splitting in many-electron atoms, where the energy level splitting (δ) is proportional to the energy level difference of a particular atom. This proportionality is the main result derived in the previous section, which is qualitatively acceptable compared to the atomic spectra listed in table 1. This proportionality is also important to study spin-orbit coupling and spin transport in spintronics materials [24,25].

6. Additional notes and conclusions

In this section we answer some of the issues that could lead to confusions. Firstly, we have successfully proved the correctness of eq. (5), which we have set out to do. The primary motivation of writing the Hamiltonian in the form of eq. (5) is that we do not need to solve the many-body Hamiltonian given in eq. (24). For example, in molecules, we can estimate the electronic excitation probability of a given molecule as compared to another molecule (with different atoms) directly from eq. (5), by applying the same procedure discussed in the section, Application I. In doing so, we can obtain the correct trend to the changes in the excitation probability of a particular molecule as compared to another molecule with different atoms. This prior knowledge will guide us to fine-tune the molecules' electronic properties to our advantage, for example, by substituting an atom with a particular atomic energy level difference in the molecule. A new mathematical formalism needs to be developed to evaluate the evolution of ξ (energy level difference) in molecules and solids for quantitative predictions. Thus far, we have used the ionization energy approximation instead, which has been very accurate and this gives us a clue to develop the required formalism. In other words, the atomic energy level difference of each constituent atom in a molecule must be a function of its band gap (highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO)).

Even though screened Coulomb potential is a crude approximation [26], we have transformed this potential to provide accurate information as given in eq. (19). In other words, note that the screening parameter (screener) (σ) is given by $\sigma = \mu \exp[-(1/2)\lambda\xi]$. Clearly, we have σ as a function of the atomic energy level difference, which is new as well as accurate as discussed previously in refs [7,18,20,25]. Hence, if we were to take σ as a mere variable, then its accuracy entirely depends on the accuracy of solutions obtained from solving eq. (24). This is the reason why the standard screened Coulomb potential is regarded as a crude approximation. In

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Table 1. The energy level difference (ξ) and the corresponding energy level splitting (δ) were calculated using the experimental data obtained from ref. [23] (eqs (44) and (45)). See text for details.

| EC | Term | J | E_L (eV) | ξ (meV) | δ (meV) |
|----------------------------|----------|---------------|------------|-------------|----------------|
| He: 1s3p | $^3P^o$ | 2 | 23.0070718 | 66.58 | 0.036 |
| | | 1 | 23.0070745 | | |
| | | 0 | 23.0071081 | | |
| He: 1s3d | 3D | 1 | 23.0736551 | | |
| He: 1s4p | $^3P^o$ | 2 | 23.7078898 | 28.20 | 0.015 |
| | | 1 | 23.7078909 | | |
| | | 0 | 23.7079046 | | |
| He: 1s4d | 3D | 1 | 23.7360912 | | |
| C: $2s^2 2p^2$ | 3P | 0 | 0.000000 | 1263.73 | 5.380 |
| | | 1 | 0.002033 | | |
| | | 2 | 0.005381 | | |
| C: $2s^2 2p^2$ | 1D | 2 | 1.263725 | | |
| C: $2s 2p^3$ | $^3D^o$ | 3 | 7.945765 | 591.33 | 0.500 |
| | | 1 | 7.946128 | | |
| | | 2 | 7.946265 | | |
| C: $2s^2 2p(2P^o)3p$ | 1P | 1 | 8.537096 | | |
| Mn: $3d^6(^5D)4s$ | a^6D | $\frac{9}{2}$ | 2.114214 | 204.96 | 72.51 |
| | | $\frac{7}{2}$ | 2.142695 | | |
| | | $\frac{5}{2}$ | 2.163713 | | |
| | | $\frac{3}{2}$ | 2.178214 | | |
| | | $\frac{1}{2}$ | 2.186728 | | |
| Mn: $3d^5(^6D)4s4p(^3P^o)$ | z^8P^o | $\frac{9}{2}$ | 2.319170 | | |
| Mn: $3d^6(^5D)4s$ | a^4D | $\frac{7}{2}$ | 2.888419 | 186.67 | 64.74 |
| | | $\frac{5}{2}$ | 2.919729 | | |
| | | $\frac{3}{2}$ | 2.940845 | | |
| | | $\frac{1}{2}$ | 2.953163 | | |
| Mn: $3d^5(^6D)4s4p(^3P^o)$ | z^6P^o | $\frac{7}{2}$ | 3.075087 | | |

contrast, in our methodology as presented here, we used the atomic spectra to obtain the atomic energy level difference, which is defined as the ionization energy (ξ) in the ionization energy approximation, which in turn gives accurate probabilities for the electronic excitations. Note here that the correct technical label for ξ is the excitation energy [18,25] in which, $\xi \propto E_I$, where E_I is the ionization energy in the ionization energy approximation.

Finally, we stress here that ξ , which is related to the excitation energy can be transformed to the ionization energy by means of the ionization energy approximation. Only within this approximation, our formalism can be related to

the Green function. For example, the Green function for the free particles can be written as $G(\mathbf{k}, \omega) = 1/(\omega - E(\mathbf{k}) + i\delta)$, where \mathbf{k} , ω , $E(\mathbf{k})$ and δ are the wavevector, energy variable, one-particle electronic energy and convergence factor, respectively [27]. Therefore, the Green function has a pole at the point, $\omega = E(\mathbf{k}) - i\delta$ and consequently, $\xi \propto E_I = \omega$, where the proportionality means that the ionization energy approximation has been invoked. By contrast, the true $\xi = \omega_{\text{GS}} - \omega_{\text{ES}} = [E(\mathbf{k}) - i\delta]_{\text{GS}} - [E(\mathbf{k}) - i\delta]_{\text{ES}}$, where GS and ES denote the ground and excited states, respectively. Apparently, ξ in the absence of the ionization energy approximation is not related to the original Green function.

In conclusion, we have established a many-body Hamiltonian with ionization energy as the eigenvalue, in which, the screened Coulomb potential operator is found to correspond qualitatively to the ionization energy eigenvalue. It is not possible to find an operator that corresponds quantitatively due to the definition of the ionization energy itself. The advantage of working with this Hamiltonian is that we do not need to solve the Hamiltonian in order to make qualitative predictions in many-electron atoms. In other words, we can use the total energy, which is the function of ionization energy in order to predict the changes in screening strength and spin-orbit separation for different atoms. Here, we have given proofs of existence by applying it to one-dimensional systems and non-relativistic atomic hydrogen exactly, while the proofs for atomic helium, and ionic lithium and beryllium do not include the complete relativistic and radiation effects. We found that the ionization energy is a mathematically and physically valid eigenvalue and its corresponding screened Coulomb potential operator is also found to be valid.

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