the external potential of the O$_2$ molecule

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This short text aims to provide an elaborate answer to the question put in the title, hopefully covering all issues you possibly might have encountered in your attempt to answer this question. Even if you answered the question correctly, going through this text might increase your understanding of what an external potential is.

Although the question is about the *external potential* of the O$_2$ molecule, the most common answer is to give the *external potential energy* of the O$_2$ molecule (let's call this *answer 1*) :

$$E_{ext} = \frac{-1}{4\pi\epsilon_0} \sum_{j=1}^{2} \sum_{i=1}^{16} \frac{8e^2}{\left|\vec{R}_j - \vec{r}_i\right|} \tag{1}$$

Verify that this has indeed the dimensions of energy (Joule), and not the dimensions of a potential (Joule per Coulomb). This answer is not necessarily wrong, as long as you know what you have written: it is the Coulomb interaction energy for two classical positive point charges at positions $\vec{R}_j$ with 16 classical negative point charges at positions $\vec{r}_i$. Or in other words: each of the 16 classical electrons feels the positive electrostatic potential provided by each of the 2 classical nuclei.

In case you did not have 2 and 16 in this expression: mind that we need to have all nuclei (2 in a diatomic molecule) and all electrons (oxygen has Z=8, hence 16 electrons for the entire molecule).

That was an energy, though, and the question was about a potential. This is the potential provided at the point $\vec{r}$ by 2 classical O-nuclei that are at positions $\vec{R}_j$ (*answer 2*):

$$V_{ext}(\vec{r}) = \frac{1}{4\pi\epsilon_0} \sum_{j=1}^{2} \frac{8e}{\left|\vec{R}_j - \vec{r}\right|} \tag{2}$$

There is no electron information in this expression, it depends entirely on the nuclei. Also, the result is not a number (as it was for answer 1), yet a function of $\vec{r}$.

In a quantum context, we meet the external potential as an operator (part of a hamiltonian). The external potential *operator* is a sum over all 16 electron positions of the previous expression (*answer 3*):

$$\hat{V}_{ext} = \sum_{i=1}^{16} V_{ext}(\vec{r}_i) \tag{3}$$

Mind the "^" on the V, which emphasizes this is an operator.

If we evaluate this operator for the wave function $\Psi(\vec{r}_1, \ldots, \vec{r}_{16})$ of the oxygen molecule, we have the quantum version of answer 1 – a quantum expression for the total electrostatic potential (*answer 4*):

$$E_{ext} = -e \left\langle \Psi \left| \hat{V}_{ext} \right| \Psi \right\rangle \tag{4}$$

(the multiplication with -e is needed to go from potential to energy – the wave function is only a probability, not a charge).

Within Density Functional Theory, the electron charge density plays an important role. All properties can be written as a functional of this density. The external potential energy (answer 4) is one of the few properties for which the exact way to do this is known (*answer 5*) :

$$E_{ext} = \int V_{ext}(\vec{r})\rho(\vec{r}) \, d\vec{r} \tag{5}$$

Herein, we recognize the $V_{ext}(\vec{r})$ from answer 2. The *charge* density $\rho(\vec{r})$ is the product of -e and the *probability* density that is obtained from the wave function.

Five answers, all of them correct if you know what you do. Which one was yours, or how and why did yours deviate from these?